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# Equilibrium binding studies of mono, di, and triisocyanide ligands on Au powder surfaces

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Equilibrium binding studies of mono, di, and triisocyanide  
ligands on Au powder surfaces

by

Allyn Ontko

A dissertation submitted to the graduate faculty  
in partial fulfillment of the requirements for the degree of  
DOCTOR OF PHILOSOPHY

Major: Inorganic Chemistry

Major Professor: Robert J. Angelici

Iowa State University

Ames, Iowa

1997

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**For the Graduate College**

*To my wife, Andrea, whose support and friendship made this work possible.*

*To Katya and David, for reminding me of the joy of discovery.*

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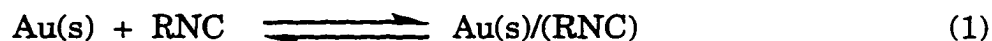
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## ABSTRACT

Our group has previously shown that isocyanides are readily adsorbed from solutions to Au powder and bind to the Au surface in an end-on fashion through the terminal carbon. Later work demonstrated that the equilibrium constants for the reversible adsorption (eq 1) of electronically inequivalent isocyanides could be obtained using the Langmuir isotherm technique. This



dissertation describes two projects completed which complement the initial findings of this group.

Initially, several alkylisocyanides ( $\text{RNC} = n\text{-C}_4\text{H}_9\text{NC}$ ,  $n\text{-C}_6\text{H}_{13}\text{NC}$ ,  $n\text{-C}_8\text{H}_{17}\text{NC}$ ,  $n\text{-C}_{12}\text{H}_{25}\text{NC}$ , and  $n\text{-C}_{18}\text{H}_{37}\text{NC}$ ) were synthesized to examine the effect of tail length on Au powder adsorption. It was observed that the length of the alkyl chain affected not only the Au surface binding affinity, but also the rate of surface saturation and saturation coverage values. Direct competition studies were also studied using a  $^{13}\text{C}$ -labeled isocyanide ( $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$ ). These studies demonstrated the stabilization afforded by substrate-substrate packing forces in SAM's formed by the longer chain isocyanides.

In a second study, di and triisocyanides were synthesized to determine the effect that the length of the connecting link (i.e. # of  $(-\text{CH}_2-)$  groups) and the number of isocyanide groups (as points of attachment) have on Au adsorption stability. Reports have shown that diisocyanides with flexible backbones such as  $\text{C}\equiv\text{N}-(\text{CH}_2)_6\text{-N}\equiv\text{C}$  and  $\text{C}\equiv\text{N}-(\text{CH}_2)_{12}\text{-N}\equiv\text{C}$  bind to Au through both  $\text{-N}\equiv\text{C}$  groups

producing a SAM with a smaller ellipsometric thickness than a diisocyanide with an inflexible backbone such as 1,4-phenylene-diisocyanide. Our work in this area describes the binding modes, relative binding affinities ( $Q_{ab}$ ) and surface coverage values for a series of flexible alkyl and xylyldiisocyanides on Au powder surfaces.

# GENERAL INTRODUCTION

## Dissertation Organization

This dissertation contains two papers written in the American Chemical Society approved publication format which describe the research performed at Iowa State University. Preceding these papers is a literature review of the chemisorption behavior of alkylthiol and alkyldithiol ligands on Au(111) surfaces. This review is intended to provide the reader with the proper perspective necessary to fully appreciate the research which follows. In the literature review as well as the papers, the literature citations, schemes, tables and figures pertain only to the chapters in which they appear. A general summary is included after the final paper.

## The Chemisorption of Alkylthiols and Alkyldithiols to Gold Film

### Introduction

Interest in self-assembled monolayers (SAM's) has grown substantially in the past decade.<sup>1-4</sup> Driving this period of discovery is the relevance of SAM's to biological interfaces and membranes, corrosion inhibition, electrochemistry, wetting, adhesion, and microelectronic circuitry.<sup>5,6</sup> This intensive examination of SAM's also contributes significantly to our more general understanding of the chemistry and physics of complex surfaces and interfaces alike. It is interesting to note, however, that the initial discovery of SAM's occurred some 50 years ago when Zisman first published his work on the preparation of a monomolecular layer by adsorption of a surfactant onto a

clean metal surface.<sup>7</sup> In his day, the potential of this work was not fully appreciated and his publication garnered only a limited level of interest.

SAM's are formed by the adsorption of molecules from a homogeneous solution onto a substrate. The organization of the SAM arises from the affinity of the 'head' group, the reactive group which chemically attaches to the substrate by covalent interaction, combined with the favorable interactions between close-packed tail groups. A successful example of this is based on the strong adsorption of thiols (RSH), disulfides (RSSH), and related species (dialkyl sulfides, alkyl xanthates, and dialkylthiocarbamates) on the noble metals (Ag, Au, and Pt). Discovery of thiol self-assembly can be attributed to work done by Allara and Nuzzo<sup>8,9</sup>, although it was a series of papers in 1987 by several groups<sup>10-14</sup> and in 1988 by Whitesides<sup>15-20</sup> that initiated numerous studies of thiol SAM's.

The strength of the bond formed between the sulfur and the gold atom, which is believed to arise from the formation of a surface thiolate (although this is still under debate), is on the order of 40-50 kcal/mol.<sup>21</sup> The high affinity of gold and other metals (i.e. Ag, Cu, Pt, Hg, and Fe) toward sulfur adsorption allows a diverse range of functional groups to be incorporated into the SAM. This combined with the ease in preparation and handling of sulfur species has led to an explosion of publications, mostly on alkylthiol SAM's, as noted by several recent review articles on the subject.<sup>1-4</sup> The remainder of this introduction describes the influence of the attached functional group on the thermodynamic and kinetic factors governing alkylthiol chemisorption to Au films.

### Characterization of *n*-alkylthiols on Au film

Due to their high degree of order and stability, SAM's of this class lend themselves to a great variety of physical and chemical characterization techniques. For simplicity, the focus of most of the information presented will be for thiol adsorption on a predominantly Au(111) surface as these are the most extensively studied systems to date. However, some studies of thiol chemisorption have also been carried out on Au(100) surfaces.<sup>22, 23</sup>

As previously noted, the bonding of the sulfur head group to the gold substrate is presumed to be in the form of a metal-thiolate.<sup>21</sup> This is a strong interaction, estimated at 40-50 kcal/mol, and the resulting SAM's are quite thermally stable. Electron diffraction<sup>20, 24</sup> and scanning tunneling microscopy (STM)<sup>25, 26</sup> studies reveal that the thiolate monolayer forms a ( $\sqrt{3} \times \sqrt{3}$ ) R30° structure (Fig. 1), which can extend over hundreds of square nanometers. The 5 Å spacing between adjacent sulfur atoms in this adlayer is almost three times that of the van der Waals diameter of a sulfur atom (3.70 Å) implying that sulfur-sulfur interactions are minimized. This distance is also greater than the distance of closest approach of the alkyl chains (4.24 Å). As a result, the chains must tilt in order to maximize their van der Waals interactions.<sup>27, 28</sup> It is assumed from this proposed structure, that the sulfur atoms reside in the threefold hollow sites of the Au(111) surface. This assumption is consistent with the placement of the thiolate sulfur on the most electron-rich surface site.<sup>29</sup>

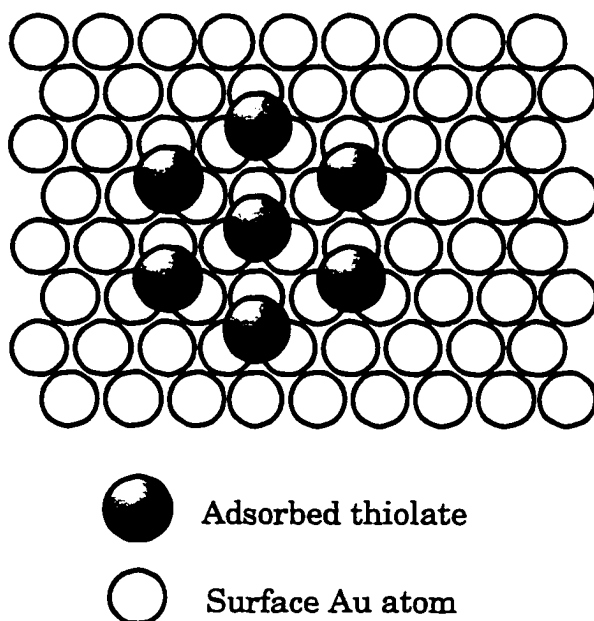


Figure 1. Example of a  $(\sqrt{3} \times \sqrt{3}) R30^\circ$  adlayer of RSH on Au(111)

The structure of the polymethylene chains of chemisorbed alkylthiols has been examined quantitatively by ellipsometry<sup>11, 30</sup>, infrared spectroscopy<sup>31, 32</sup>, Raman spectroscopy<sup>33</sup>, and numerous other techniques<sup>34-36</sup>. These methods all describe a binding scheme in which the alkyl chains are fully extended, tilted with respect to the surface normal, and in a nearly all-*trans* configuration. Molecular dynamics simulations<sup>37</sup> as well as molecular mechanics calculations<sup>27</sup> also support these findings. To date, all reported measurements of adsorbed thiols on Au demonstrate linear changes in film thickness with increasing polymethylene chain length.<sup>11, 30, 32, 38</sup> Also, progression bands, which are only seen when aliphatic chains occur in an all-*trans* configuration, were observed in the low frequency infrared spectra for chemisorbed  $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{CH}_3$ .<sup>31</sup> This finding further suggests that a strong

correlation exists between the chain conformations in the monolayer and in the bulk, crystalline material.

Infrared spectroscopy probably provides the best evidence for the structure of polymethylene chains of adsorbed alkylthiols. A report by Nuzzo et al.<sup>31</sup> suggested that the chains are fully extended and reside in a crystalline-like environment based on the width and position of the asymmetric  $\text{CH}_2$  stretching vibration ( $2918\text{ cm}^{-1}$ ) of *n*-hexadecanethiol on Au film. He further concluded from this spectroscopic information that if there were significant numbers of *gauche* defects in the overlayer, or if it were not tightly packed, then the position of this band would shift to higher frequency and its width would broaden substantially. He further concluded that the relative intensities of the symmetric and orthogonal asymmetric polymethylene stretching vibrations imply that the chains must also be tilted with respect to the surface normal.<sup>31</sup> This tilt angle has been calculated by a number of research groups using infrared<sup>31, 39</sup> and Raman<sup>33</sup> data and is expected to be optimized at 25-30°. It should be noted that in the examination of mixed SAM's containing two different thiols with two different alkyl chain lengths, the shorter chain species appears well oriented with few *gauche* defects while the longer chain component appears more disordered.<sup>40</sup> This observation suggests that two component monolayers are generally mixed at the molecular level.

Surface infrared techniques have also been shown to be useful for monitoring the orientation of non-alkane moieties buried in the hydrocarbon network.<sup>41-46</sup> The solvent incorporation in SAM's is of considerable interest to electrochemists as solvents may be able to penetrate the insulating region of



the monolayer. Porter et al.<sup>47</sup> obtained IR spectra of an *n*-octadecanethiol SAM in contact with several solvents (D<sub>2</sub>O, CD<sub>3</sub>OD, and CCl<sub>4</sub>). They noted that disorder primarily occurred at the terminal methyl group and concluded from this finding that penetration of solvent into the methylene region of the monolayer was unlikely. Whitesides also supports this finding in citing that SAM contact with water only modestly perturbs the structure of an alkylthiolate SAM.<sup>40</sup> Bain and coworkers employed a different technique, sum-frequency generation, to *n*-octadecanethiol on Au film and found that immersion of a SAM into solution produced little effect on the SAM; except hexane, which produce slight disorder.<sup>48</sup>

#### **Kinetic and thermodynamic factors affecting the adsorption of alkylthiols on Au(111) surfaces**

Kinetic studies of alkylthiol adsorption onto Au films have shown that in relatively dilute solution, two distinct adsorption rates can be observed.<sup>30</sup> The first, a very fast step, occurs in seconds to minutes and produces a monolayer which has measured contact angles close to their limiting values and a measured film thickness of 80-90% of maximum. This step, described well by diffusion-controlled Langmuir adsorption, was found to depend strongly on thiol concentration.<sup>30</sup> At a solution concentration of 1 mM this step is completed in approximately 1 minute while it requires over 100 minutes to produce the same coverage from a 1  $\mu$ M solution.<sup>30</sup> The second, slower step, which lasts for several hours, produces SAM's with complete (100%) surface coverage and maximum thickness. This slower step is concluded to be a surface crystallization process where alkyl chains order to form a quasi two-

dimensional crystal on the surface. It follows that the kinetics of the first step is governed by the rate of oxidative addition of the sulfur head group, which is dependent on the electron density at the sulfur. On the other hand, the kinetics of the second step may be related to chain disorder (the aforementioned *gauche* defects would be one such example) and the different components of substrate-substrate interactions (like the attractive van der Waals' forces).

Such kinetic effects were observed during competition studies between long and short chain alkylthiols.<sup>49</sup> The more rapid SAM formation by short chain thiols was noted when long and short tailed species were competed directly from several different solvents. It was also noted in these studies that the absorption isotherms obtained for the competition of C<sub>22</sub>SH and C<sub>12</sub>SH were quite different for isooctane and ethanol solvents. The authors offered little kinetic evidence to support the large difference in solvent influence, but did, however, offer the hypothesis that thermodynamically, the greater preference for the adsorption of the longer chain from ethanol was the direct consequence of the poorer solvation of the hydrocarbon chain in ethanol as compared to isooctane. Also, it was noted that the surface composition changed with time; more long chain thiol displaced short chained thiol on the surface with time. The preference for the adsorption of the longer chain thiol after long contact times was most easily reconciled with predominantly thermodynamic control of the composition of the monolayer. It was then concluded that, as described above, the rapid adsorption process favored the adsorption of the short chained thiol (the kinetic product) which was then displaced in favor of the more

thermodynamically stable long chain thiol. Again, the thermodynamic stability afforded by substrate-substrate packing was presumed to be the major contributor.

The consensus description for the adsorption of alkylthiols on Au film states that alkyl chains longer than 10 methylene units appear to be in a quasi-crystalline state at room temperature, while shorter chain species behave more liquid-like which may be responsible, in part, for the thermodynamic stability of the subsequent SAM's formed by such adsorbates. A scanning tunneling microscopy (STM) study found that shorter chain alkylthiols ( $\text{CH}_3(\text{CH}_2)_{3-9}\text{SH}$ ) produced SAM's with distinct domain boundaries which appeared to run in the next-nearest neighbor direction as was expected to maximize van der Waals interactions.<sup>50</sup> These images were quite stable and remained unchanged after repeated scanning. It was observed during stability studies that the longer chained of the thiols studied ( $\text{C}_8\text{SH}$  and  $\text{C}_{10}\text{SH}$ ) could survive high vacuum conditions for one month, while the shorter chain thiols were more liquid-like and underwent slow loss from the surface with time.<sup>51</sup> This finding supports data obtained from the infrared spectroscopy studies in that the longer chain alkylthiols appear to be quasi-crystalline when adsorbed to Au films. The observation of this crystalline state of the SAM, which follows the slow annealing process in which the surface optimizes substrate packing interactions, is intrinsic to the stability of the alkylthiol SAM.

It is interesting to note that while numerous studies have been undertaken to understand the factors which influence thiol and disulfide chemisorption on Au film, only one quantitative report of thermodynamic data

exists to date.<sup>52</sup> A study by Schlessner et al.<sup>52</sup> recently reported the temperature and adsorbate concentration dependence of alkylthiol-Au SAM formation *in situ* using a quartz crystal microbalance (QCM). Although their work noted that there were two distinct rates of thiol adsorption attributable to the fast thiol-Au reaction and the slow annealing of alkyl tails, they focussed their kinetic and thermodynamic studies on the initial fast kinetic process. Thus, their QCM-based kinetic studies produced only information about thiol head group adsorption and make the assumption that the fast and slow processes for thiol adsorption are significantly decoupled. Also, the temperature dependence of the observed rate constant for a fixed thiol concentration demonstrated that the rate was clearly not diffusion controlled.

Using the ratio of the forward and back rates, equilibrium constants were obtained for *n*-octadecanethiol adsorption at several temperatures and subsequently used in a Van't Hoff plot to determine the enthalpy ( $\Delta H_{\text{ads}} = -20$  kcal/mol) and entropy ( $\Delta S_{\text{ads}} = 48$  cal/mol·K) of adsorption. The data they obtained for this process suggested that the comparatively small free energy of adsorption for this process ( $\Delta G_{\text{ads}} = -5.72$  kcal/mol at 298K) is the result of a close balance between the enthalpic driving force and an entropic penalty associated with the process of self assembly. Also, the value obtained for the enthalpic term was significantly lower than the early estimates of 40-50 kcal/mol. This may be due in part to the use of hexane as a solvent for this work or due to the omission of the substrate packing forces, which have also been considered to be a significant thermodynamic contributor to thiol chemisorption on Au.

SAM's formed by the adsorption of *n*-octadecanethiol to metal surfaces have been shown to be quite thermodynamically stable. Examples of this stability have also been demonstrated on metal surfaces other than Au. An example of this stability include a study in which a silver surface coated with octadecanethiolate monolayers could be kept in ambient conditions without tarnishing for many months,<sup>53</sup> while even better protection was afforded by octadecanethiolate on copper surfaces which sustained nitric acid contact without notable damage.<sup>4</sup> It is clear that alkylthiol monolayers form a protective coating on Au and other metal surfaces. The ability to change of the functional group attached to the thiol also allows great diversity in resultant SAM's, each with the potential for many unique applications.

#### **Adsorption of dithiols to Au film surfaces**

Attempts to stabilize SAM's for the purpose of coating a surface could be found in increasing the number of points of attachment. It seems likely that if an alkylthiol binds strongly to an Au surface, that alkyldithiols should provide a SAM with high surface coverages and possibly, greater stability. Recent reports of dithiol adsorption to Au surfaces involves either the adsorption of a polymer which has been functionalized with thiol side chains,<sup>54</sup> or the formation of a dithiol with only one surface attached sulfur.<sup>55, 56</sup>

The recent reports of dithiol adsorption to Au films describe the use of rigid dithiols as molecular wires for electron transfer to a species attached at the non-surface bound thiol group rather than as a surface protectant.<sup>55, 56</sup> These reports have concluded that SAM's need not be comprised of alkyl groups to promote a SAM with a high packing density. The adsorption rates

for dithiols were also reported to be much slower than that observed for their alkylthiolate analogues, probably due to the bulky linking group (such as staffanes or 1,4-substituted phenyl groups) necessary to allow one end to remain unreacted upon Au adsorption.<sup>55</sup> To date, no thermodynamic stability data have been reported for dialkylthiols, but the area of research involving the use of rigid adsorbates to tether electron donor-acceptor complexes such as  $\text{Ru}(\text{NH}_3)_5^{\text{II, III}}$  to Au electrodes appears to be growing rapidly.

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# EFFECTS OF ALKYL CHAIN LENGTH ON THE ADSORPTION OF *n*-ALKYL ISOCYANIDES (RNC) ON GOLD POWDER

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## Abstract

The chemisorption of the alkyl isocyanides *n*-butyl ( $C_4H_9NC$ ), *n*-hexyl ( $C_6H_{13}NC$ ), *n*-octyl ( $C_8H_{17}NC$ ), *n*-dodecyl ( $C_{12}H_{25}NC$ ), and *n*-octadecylisocyanide ( $C_{18}H_{37}NC$ ) on Au powder from 1,2-dichloroethane (DCE) was examined using both solution (FT-IR) and surface (Diffuse Reflectance Infrared Fourier Transform or DRIFT) spectroscopic techniques. Measured values for the isocyanides with fewer than 12 carbon units in their alkyl tail show that the equilibrium binding constant ( $K_1$ ), surface coverage ( $n_{1s}$  and  $n_a$  mol/g<sub>Au</sub>), and qualitative rate of solution-surface equilibrium in DCE solvent are the same. Competition studies between  $^{13}C$  labelled  $C_{18}H_{37}NC$  and non-labelled  $C_4H_9NC$  suggest that increasing the length of the alkyl tail increases the thermodynamic stability of these RNC on Au powder; the ratio of adsorbed isocyanide at equilibrium,  $C_{18}H_{37}N^{13}C/C_4H_9NC$ , was found to be 4.1. DRIFT spectroscopy of RNC on Au powder shows that isocyanides are bound strongly to the surface at low coverages (less than 70% of saturation coverage) and this binding affinity decreases at higher coverages. Studies conducted for  $C_{18}H_{37}NC$  and  $C_4H_9NC$  in *n*-decane, DCE, and nitromethane (MeNO<sub>2</sub>) solvents

also show that solvent polarity affects the rate of monolayer formation, surface coverage, and surface binding strength.

## Introduction

The spontaneous adsorption of organic substrates on surfaces to form self-assembled monolayers (SAM's) has become an area of active interest in recent years.<sup>1</sup> One particularly versatile system, adsorbed alkyl- or arylthiols (RSH) on noble metal ( $\text{Ag}^2$  or  $\text{Au}^{3-13}$ ) surfaces, has become the focus of numerous studies for their possible relevance to corrosion inhibition, lubrication, optical devices and bio-sensors.<sup>14</sup> The ability of these SAM's to function in such applications depends in part on their strength of RSH binding to the surface. In an early investigation,<sup>7</sup> the effect of the R group chain length of the *n*-alkylthiols,  $n\text{-C}_{12}\text{H}_{25}\text{SH}$  and  $n\text{-C}_{22}\text{H}_{45}\text{SH}$ , on their adsorption to Au film was studied. When a Au film was immersed in an isooctane solution containing these thiols in molar ratios ranging from 0.01 to 1.0 ( $n\text{-C}_{12}\text{H}_{25}\text{SH}/n\text{-C}_{22}\text{H}_{45}\text{SH}$ ) the long-chain thiol adsorbed preferentially. Using C/Au ratios obtained from XPS data of the adsorbed thiols, the ratio of  $[\text{C}_{22}]_{\text{surf}}[\text{C}_{12}]_{\text{sol}}/[\text{C}_{12}]_{\text{surf}}[\text{C}_{22}]_{\text{sol}}$  was calculated to be 2.3. Preferential adsorption of  $n\text{-C}_{22}\text{H}_{45}\text{SH}$  was ascribed to van der Waals' attractions between the long alkyl chains in the ordered SAM on the Au surface. Similarly, the  $[\text{C}_{19}]_{\text{surf}}[\text{C}_{11}]_{\text{sol}}/[\text{C}_{11}]_{\text{surf}}[\text{C}_{19}]_{\text{sol}}$  ratio was estimated to be 5 when  $\text{HOC}_{19}\text{H}_{39}\text{SH}$  and  $\text{HO-C}_{11}\text{H}_{22}\text{SH}$  were coadsorbed from the polar solvent ethanol

A recent Atomic Force Microscopy (AFM) study examined substrate-substrate interactions between alkyl groups of *n*-alkylthiols adsorbed on Au film.<sup>15</sup> Two experiments were the focus of this work: a study of domain

formation by individual *n*-alkylthiols at initial stages of SAM formation and a study of the coadsorption of two *n*-alkylthiols ( $C_4H_9SH$  and  $C_{18}H_{37}SH$ ) over varying times and solution concentration ratios. In the first experiment, Au film was immersed into a 0.01 mM ethanol solution containing a single *n*-alkylthiol ( $C_4H_9SH$ ,  $C_{12}H_{25}SH$ , or  $C_{18}H_{37}SH$ ). In all cases, film coverage increased with immersion time until a maximum coverage was achieved (after about 3 minutes). In the case of the two long-chain thiols,  $C_{12}H_{25}SH$  and  $C_{18}H_{37}SH$ , island formation of thiol on the Au surface was observed by AFM while the short-chain thiol,  $C_4H_9SH$ , formed mesh-like domains. From these images, it was determined that the adsorption rate of the short-chain thiols was faster than that of the long-chain thiols, at least at the early stages of SAM formation. The authors concluded that initial SAM formation of *n*-alkylthiols on Au film is a diffusion-controlled process which should indeed favor the chemisorption of the short-chain species.

In the second experiment, Au film was immersed for 1 h in ethanol solutions containing varying molar ratios of  $C_4H_9SH$  and  $C_{18}H_{37}SH$ . AFM studies of the resulting SAM's showed that a homogeneous film of only  $C_{18}H_{37}S/Au$  was formed when  $C_4H_9SH:C_{18}H_{37}SH$  ratios of 1:1 and 10:1 were used in solution. Preferential  $C_{18}H_{37}SH$  adsorption was again attributed to van der Waals' attractive forces between the long  $C_{18}H_{37}$  groups. At ratios of 20:1 and 40:1, clear domains were observed indicating the existence of a mixed monolayer containing both *n*-alkylthiols. Solutions containing high concentrations of the short-chain competitor (100:1 ratio) produced a SAM containing only  $C_4H_9S/Au$  as evidenced by the lack of clear domain boundaries.

It was also noted that the surface composition changed with time; the long-chain thiol ( $C_{18}H_{37}SH$ ) displaced the short-chain thiol ( $C_4H_9SH$ ) on the surface with time. The preference for the adsorption of the long-chain thiol after long contact times was most easily reconciled with predominantly thermodynamic control of the composition of the monolayer.

Recently, the determination of equilibrium binding constants for the adsorption of a thiol,  $C_{18}H_{37}SH$ , on Au film was accomplished using the quartz crystal microbalance (QCM) technique.<sup>16</sup> By measuring the kinetic rates of the forward and back reactions for thiol chemisorption from *n*-hexane solutions,  $K_{eq}$  values were obtained, which yielded  $\Delta H_{ads}$  and  $\Delta S_{ads}$  values of -20(1) kcal/mol and -48(1) cal/(mol K), respectively. The heat of solvation,  $\Delta H_{solv}$ , of the thiol in solution contributes significantly to the  $\Delta H_{ads}$  of chemisorption of alkylthiols on Au and this term is both thiol- and solvent-dependent. Thus, the measured adsorption enthalpy ( $\Delta H_{ads} = -20$  kcal/mol) consists of both the solvation enthalpy ( $\Delta H_{solv} = -8$  kcal/mol, estimated) and the monolayer formation enthalpy ( $\Delta H_{ml} = -28$  kcal/mol) for this system. As the enthalpy of monolayer formation was assumed to be determined predominantly by the formation of the Au-S bond under the short-times of the measurement, the  $\Delta H_{ml}$  term would contain only a small contribution from attractive forces between the alkyl tails.

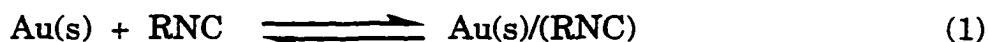
While studies of *n*-alkylthiols on Au indicate that longer *n*-alkyl groups increase binding of the thiol to the surface, there are few data that establish the magnitude of this effect. Temperature-programmed desorption (TPD) studies<sup>17</sup> of *n*- $C_{16}H_{33}SH$  on Au(111) indicate that van der Waals' attractions

between alkyl chains are approximately 0.8 kcal/mol of  $\text{CH}_2$  groups. This suggests that the difference of 14  $\text{CH}_2$  groups between  $\text{C}_4\text{H}_9\text{SH}$  and  $\text{C}_{18}\text{H}_{37}\text{SH}$  would stabilize the  $\text{C}_{18}\text{H}_{37}\text{SH}$  monolayer formation by 11 kcal/mol. Thus, equilibrium constants for the binding of the long-chain thiol should be many orders of magnitude larger than that of  $\text{C}_4\text{H}_9\text{SH}$ . Because of the difficulties inherent in measuring the equilibrium binding constants for *n*-alkylthiols on Au, we turned to studies of *n*-alkylisocyanides on Au.

There are few prior reports concerning the adsorption of isocyanides<sup>5, 18, 19</sup> on noble metal surfaces. In a previous study reported by this group,<sup>20</sup> isocyanides ( $\text{CNPh}$ , 1,4- $(\text{CN})_2\text{C}_6\text{H}_4$ ,  $\text{CNBu}^t$ ) were adsorbed from methanol solution onto Au powder and examined using diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS). These adsorbed isocyanides displayed a single  $\nu(\text{NC})$  peak shifted  $70\text{ cm}^{-1}$  to higher energy from that of the free isocyanide, which indicates that the isocyanides bind to a single surface Au atom through the isocyanide carbon atom. The amounts of the isocyanides adsorbed were shown to increase as the concentration of the isocyanide in solution increased; at high concentrations, the Au surface became saturated with isocyanide.<sup>20</sup> Further studies<sup>21</sup> showed that isocyanide surface coverage at saturation decreases ( $\text{Bu}^n\text{NC} > \textit{c}\text{-C}_6\text{H}_{11}\text{NC} > \text{Bu}^t\text{NC} > 2,4,6\text{-C}_6\text{H}_2(\text{Bu}^t)_3\text{NC}$ ) as the size of the  $\text{R-N}\equiv\text{C}$  alkyl or aryl group increases. The ratio of  $\text{R-N}\equiv\text{C}$  to surface Au atoms ranged from 1/3.9 for  $\text{CNBu}^t$  to 1/10 for 2,4,6- $\text{CN-C}_6\text{H}_2(\text{Bu}^t)_3$ . Langmuir isotherm studies<sup>21</sup> showed that the equilibrium binding constant,  $K_1$ , was greater for the adsorption of  $\text{CNPh}$  ( $27 \times 10^3$ ) than for 4- $\text{CNC}_6\text{H}_4\text{NO}_2$  ( $12 \times 10^3$ ) from 1,2-dichloroethane (DCE) solvent. The ability to use infrared

spectroscopy to monitor the isocyanide-gold chemisorption equilibrium makes these systems well-suited for the quantitative study of electronic, steric, and alkyl-chain length binding effects.

The purpose of the present study was to determine equilibrium binding constants,  $K_1$ , (eq 1) for the adsorption of a series of *n*-alkylisocyanides with



$\text{R-N}\equiv\text{C} = n\text{-C}_4\text{H}_9\text{NC}, n\text{-C}_6\text{H}_{13}\text{NC}, n\text{-C}_8\text{H}_{17}\text{NC}, n\text{-C}_{12}\text{H}_{25}\text{NC}, \text{ and } n\text{-C}_{18}\text{H}_{37}\text{NC}$

varying chain lengths on Au. Gold powder, rather than film, was chosen because the high relative surface area allows accurate measurement of the amounts of adsorbed isocyanides in the equilibrium studies. We also determined the effect of solvent on  $K_1$  values, the amounts of the *n*-alkylisocyanides adsorbed at saturation coverage, the existence of two different adsorption regimes, and shifts in  $\nu(\text{NC})$  as a function of surface coverage.

## Experimental Section

**General Procedure.** All manipulations were performed in air unless otherwise stated. All solvents including 1,2-dichloroethane (DCE) were reagent or HPLC grade and used as purchased. The starting materials *n*-hexylamine, *n*-octylamine, *n*-dodecylamine, *n*-octadecylamine, and benzyltriethylammonium chloride were purchased from Aldrich and used as received. Purchased *n*-butylisocyanide (Aldrich) was vacuum distilled and

checked for purity ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR and FTIR) prior to use. The Au powder for this work was prepared as described previously.<sup>22</sup>

The  $^1\text{H}$  NMR spectra were obtained on samples in  $\text{CDCl}_3$  solvent using a Nicolet-NT 300 MHz spectrometer with TMS as the internal reference ( $\delta=0.00$  ppm). The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were obtained on samples in  $\text{CDCl}_3$  solvent using a Varian VXR-300 MHz spectrometer with  $\text{CDCl}_3$  as the internal standard ( $\delta=77.06$  ppm). All infrared spectra were recorded on a Nicolet 710 spectrophotometer equipped with a TGS detector in the main compartment and an MCT detector in the auxiliary experiment module (AEM). The AEM housed a Harrick diffuse reflectance accessory. All solution IR spectra were recorded using a NaCl cell (1.0 mm) in the main compartment with the instrument set for  $4\text{ cm}^{-1}$  resolution and 128 scans. All DRIFT spectra, using 256 scans and  $4\text{ cm}^{-1}$  resolution, were recorded on samples in the Harrick microsampling cup. The background spectrum used for the DRIFT spectra was taken on clean gold powder. Spectra were routinely baseline- and purge-corrected. Kubelka-Munk transformations of the DRIFT spectra were not possible due to the low intensities of all bands (i.e., the bands were eliminated by the transformation).

**Cleaning of Au Powder.** Clean Au for the chemisorption studies was prepared by treating 10 - 20 g of Au powder used in previous RNC adsorption studies with 50 mL of freshly prepared 'piranha' solution comprised of a 50/50 mixture of conc.  $\text{H}_2\text{SO}_4$  and 30% aqueous  $\text{H}_2\text{O}_2$  (caution: add  $\text{H}_2\text{SO}_4$  to  $\text{H}_2\text{O}_2$ ) in a large beaker with slow stirring. Vigorous foaming and gas evolution



occurred for 5 min. Nitrogen was blown over this reaction to reduce gold loss due to foaming. The mixture was allowed to stir for 15 additional min and was then diluted with 250 mL of distilled water. The gold was filtered on a coarse frit, washed ten times with 50 mL aliquots of water followed by five 50 mL methanol washings, and dried under a nitrogen stream with stirring. The Au powder was then baked overnight in a 160°C oven. DRIFT spectra of Au powder treated in this manner showed no evidence of adsorbed isocyanide as indicated by the absence of absorptions in the  $\nu(\text{C-H})$  and  $\nu(\text{NC})$  regions. Routine BET surface area measurements of the Au powder were performed on a Micromeritics AccuSorb 2100E instrument using Kr as the adsorbing gas at 77 K. The measured surface area of the Au powder used in these studies was  $0.33 \pm 0.03 \text{ m}^2/\text{g}$ . The numerous treatments with piranha solution have little effect on the surface area of the Au powder. After more than 20 of these treatments, maximum coverages obtained for all isocyanides studied showed a decrease of approximately 10% with no measurable effect on  $K_1$ . Series of studies were performed with the same batch of Au powder.

**Synthesis of *n*-alkylisocyanides (RNC).** The compounds *n*-hexyl, *n*-octyl, *n*-dodecyl, and *n*-octadecylisocyanide were synthesized using a slightly modified version of Procedure B outlined by Weber et al.<sup>23</sup> This route to isocyanides utilizes the phase transfer catalysis method of generating dihalocarbenes from chloroform and 50% aqueous NaOH. All reactions were carried out on a 50 mmol scale based on the primary amine. The following describes the alterations made to the published route:<sup>23</sup> After separation and drying of the organic phase over  $\text{K}_2\text{CO}_3$ , the volatiles were removed from the

organic solution by vacuum. The resulting oil (usually orange/brown) was then dissolved in 25 mL of hexanes, and the solution was chromatographed on a 2 x 20 cm silica column (40  $\mu\text{m}$  silica particle size, Scientific Adsorbents Inc.) by eluting with hexanes. Fractions from the column were monitored by FTIR spectroscopy for isocyanide ( $\nu(\text{NC}) = 2146 \text{ cm}^{-1}$  in hexanes) and collected upon detection. Removal of hexanes under vacuum at 25°C produced spectroscopically ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR and FTIR) pure isocyanides in low to moderate yields (10-30%). Chromatography was the chosen method for purification as polymerization of the isocyanides often occurred during the recommended<sup>23</sup> fractional distillation.

All of the isocyanides were isolated as colorless liquids at room temperature; octadecylisocyanide is a white solid at temperatures below 20°C. Yield and characterization data for each isocyanide are given below. For the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectral data, only NC and  $\alpha$ -methylene carbon chemical shifts are listed; the remaining carbons in the alkyl chain occurred in the expected chemical shift regions for aliphatic hydrocarbons ( $\delta=19\text{-}32 \text{ ppm}$  for  $\text{CH}_2$  and  $\delta=13\text{-}14 \text{ ppm}$  for  $\text{CH}_3$ ) and were not individually assigned. The  $^{13}\text{C}$ -labeled *n*-octadecylisocyanide ( $\text{C}_{18}\text{H}_{37}\text{N}\equiv^{13}\text{C}$ ) used in the competitive binding studies was prepared following the identical procedure as the non-labeled *n*-octadecylisocyanide using  $^{13}\text{CHCl}_3$  (Cambridge Isotopes Inc.) instead of  $\text{CHCl}_3$ .

***n*-Hexylisocyanide ( $\text{C}_6\text{H}_{13}\text{NC}$ ).** 17% yield. IR (DCE):  $\nu(\text{NC}) 2150 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  3.31 (tt,  $J_{\text{HH}}=6.6 \text{ Hz}$ ,  $J_{\text{HN}}=2.0 \text{ Hz}$ , 2H,  $\alpha\text{-CH}_2$ ), 1.60 (m, 2H,  $\beta\text{-CH}_2$ ), 1.37 (m, 2H,  $\gamma\text{-CH}_2$ ), 1.27 (m, 4H, remaining  $\text{CH}_2$  units), 0.84 (t,  $J_{\text{HH}}=6.6 \text{ Hz}$ , 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  155.6 (t,  $J_{\text{CN}}=5.5 \text{ Hz}$ , -NC), 41.4 (t,  $J_{\text{CN}}=6.3 \text{ Hz}$ ,  $\alpha\text{-CH}_2$ ).

***n*-Octylisocyanide (C<sub>8</sub>H<sub>17</sub>NC).** 28% yield. IR (DCE):  $\nu(\text{NC})$  2150 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  3.36 (tt,  $J_{\text{HH}}=6.6$  Hz,  $J_{\text{HN}}=1.8$  Hz, 2H,  $\alpha$ -CH<sub>2</sub>), 1.65 (m, 2H,  $\beta$ -CH<sub>2</sub>), 1.41 (m, 2H,  $\gamma$ -CH<sub>2</sub>), 1.27 (m, 8H, remaining CH<sub>2</sub> units), 0.87 (t,  $J_{\text{HH}} = 6.3$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  155.5 (t,  $J_{\text{CN}}=5.5$  Hz, -NC), 41.5 (t,  $J_{\text{CN}}=6.4$  Hz,  $\alpha$ -CH<sub>2</sub>).

***n*-Dodecylisocyanide (C<sub>12</sub>H<sub>25</sub>NC).** 27% yield. IR (DCE):  $\nu(\text{NC})$  2150 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  3.36 (tt,  $J_{\text{HH}}=6.6$  Hz,  $J_{\text{HN}}=1.8$  Hz, 2H,  $\alpha$ -CH<sub>2</sub>), 1.64 (m, 2H,  $\beta$ -CH<sub>2</sub>), 1.39 (m, 2H,  $\gamma$ -CH<sub>2</sub>), 1.25 (m, 16H, remaining CH<sub>2</sub> units), 0.87 (t,  $J_{\text{HH}} = 6.3$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  155.6 (t,  $J_{\text{CN}}=5.6$  Hz, -NC), 41.4 (t,  $J_{\text{CN}}=6.4$  Hz,  $\alpha$ -CH<sub>2</sub>).

***n*-Octadecylisocyanide (C<sub>18</sub>H<sub>37</sub>NC).** 28% yield. IR (DCE):  $\nu(\text{NC})$  2150 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  3.36 (tt,  $J_{\text{HH}}=6.6$  Hz,  $J_{\text{HN}}=1.8$  Hz, 2H,  $\alpha$ -CH<sub>2</sub>), 1.65 (m, 2H,  $\beta$ -CH<sub>2</sub>), 1.41 (m, 2H,  $\gamma$ -CH<sub>2</sub>), 1.24 (m, 28H, remaining CH<sub>2</sub> units), 0.86 (t,  $J_{\text{HH}} = 5.7$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR:  $\delta$  155.9 (t,  $J_{\text{CN}}=5.3$  Hz, -NC), 41.5 (t,  $J_{\text{CN}}=6.4$  Hz,  $\alpha$ -CH<sub>2</sub>).

**General Procedure for Adsorption Studies of *n*-alkylisocyanides on Au Powder.** Isocyanide solutions for a series of adsorption studies were prepared by serial dilution of a 20 mM stock solution. Then, a 1.00 mL aliquot of the desired concentration of isocyanide was added to a 16 mm Pyrex test tube containing 500 mg of clean Au powder. The sample tube was capped tightly with a teflon-lined screw-cap, shaken on a Vortex Genie 2 mixer (Fisher) equipped with a 4-tube platform attachment, and allowed to settle undisturbed. For all Langmuir isotherm studies, mixing times beyond 5 min produced no change in surface coverage. After 24h (*n*-butyl, -hexyl, -octyl, and -dodecyl) or 72h (*n*-octadecyl) of settling, a sample of the solution over the gold powder was withdrawn from each tube by syringe. The concentration of the RNC in the solution was analyzed by FTIR spectroscopy using the  $\nu(\text{NC})$  band intensity.

The Au powder from each sample was filtered from the remaining solution using a Buchner funnel. Exactly 50 mg of filtered Au powder was then introduced through a micro funnel into a microsampling cup for DRIFT analysis. A typical series of measurements for Langmuir isotherm plots required 6 to 14 solutions which were each analyzed as described above. All procedures were performed at room temperature.

## Results

**General Adsorption Studies.** Correlation coefficients for Beer-Lambert plots of  $\nu(\text{NC})$  absorbances versus RNC solution concentrations (standard error is 0.01 mM) in the concentration range studied (0.10-10 mM) are 0.9999 or higher in DCE, *n*-decane, and nitromethane solvents. Calculated extinction coefficients,  $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ ), are given in Tables 1 and 2. These  $\epsilon$  values were then used to determine the concentration (mM) of RNC,  $[\text{C}]$ , remaining in solution after stirring with Au powder and the initial solution concentration (mM) of RNC,  $C_{\text{initial}}$ . The amount of RNC adsorbed on the Au surface,  $S$  (mol RNC/g<sub>Au</sub>), was then calculated as the amount of RNC lost from 1.00 mL of solution,  $(C_{\text{initial}} - [\text{C}])(1.00 \text{ mL})$ , per g of Au powder used.<sup>21</sup>

A plot of either  $\Delta C$  ( $C_{\text{initial}} - [\text{C}]$ ) or  $S$  versus  $C_{\text{initial}}$  demonstrates typical Langmuir behavior<sup>24</sup> for all *n*-alkylisocyanides in all solvents (Figure 1.). From these plots, the maximum surface coverage,  $n_a$  (mol RNC/g<sub>Au</sub>), was obtained using the asymptotic value of  $S$ . For a given isocyanide and solvent,  $n_a$  is the same for several separate sample sets and is unaffected by  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  treatment of the Au powder. DRIFT spectroscopic studies of Au

powder with a saturation coverage of RNC shows a  $\nu(\text{NC})$  band for all isocyanides at  $2223\text{ cm}^{-1}$  which is about a  $70\text{ cm}^{-1}$  shift to higher energy from that ( $2150\text{ cm}^{-1}$ ) of the isocyanide in solution. The absence of a  $\nu(\text{NC})$  band at  $2145\text{-}2155\text{ cm}^{-1}$  indicates that there is no physisorbed RNC on the Au surface.

**Qualitative Kinetic Behavior.** In order to ensure that equilibrium was achieved in measurements of equilibrium constants,  $K_1$ , in eq 1, the following experiments were performed. By syringe,  $1.00\text{ mL}$  of a  $3.0\text{ mM}$  RNC solution was added to a series of tubes (usually 8-12) each containing  $300\text{ mg}$  of Au powder. These samples were then capped, stirred, and allowed to settle undisturbed. A solution sample was withdrawn from a different tube at regular intervals. FTIR analysis of the solution began immediately after  $5\text{ min}$  of stirring and ended after a settling period of  $5\text{ days}$ . Values of  $S$  approached an asymptotic limit with time for all isocyanides in all solvents. Changing the amount of Au powder used or the test tube diameter did not measurably affect the time required to achieve equilibrium. Plots of coverage ( $S$ ) versus time (min after mixing) revealed that a  $24\text{ h}$  settling period was necessary to establish equilibrium for the adsorption from solution of all isocyanides except  $\text{C}_{18}\text{H}_{37}\text{NC}$ , which required approximately  $72\text{ h}$ .

A qualitative comparison of adsorption rates was also investigated using isocyanides with the shortest and longest alkyl chains ( $\text{C}_4\text{NC}$  and  $\text{C}_{18}\text{NC}$ ) in solvents of differing polarities; their dielectric constants<sup>25</sup> decrease in the following order:  $\text{MeNO}_2$  (30) > DCE (10) > *n*-decane (2). Plots (Fig. 2) of coverage ( $S$ ) versus time (h after mixing) for both the *n*-butyl and *n*-octadecyl-

isocyanides show that the time required to achieve saturation coverage decreases with the solvent in the following order:  $\text{MeNO}_2 > n\text{-decane} > \text{DCE}$ . However, they also show that the times required to reach a coverage of approximately  $1.5 \times 10^{-6} \text{ mol/g}_{\text{Au}}$  are essentially the same for all three solvents. While little additional RNC adsorbs beyond this point from DCE solvent, more RNC adsorbs from  $n\text{-decane}$ , and still more from nitromethane. The adsorption beyond  $1.5 \times 10^{-6} \text{ mol/g}_{\text{Au}}$  occurs at a much slower rate. It is not clear why the saturation surface coverage is greater in  $\text{MeNO}_2$ ; however, one might speculate that this polar solvent is less strongly associated with the  $n$ -alkyl chains than the less polar  $n\text{-decane}$  and DCE. Thus, the occluded  $\text{MeNO}_2$  is displaced by additional isocyanide, which occurs at a relatively slow rate. For the case of DCE, where little additional isocyanide adsorbs, significant amounts of the solvent presumably remain incorporated in the adsorbed isocyanide layer.

**Langmuir Treatment of Adsorption Data.** The quantitative determination of relative binding affinities of the  $n$ -alkylisocyanides makes use of the Langmuir equation (eq 2).<sup>21, 24</sup> In this equation,  $K_1$  is the equilibrium constant

$$K_1 = S/[C](n_{1s} - S) \quad (2)$$

for the adsorption of the isocyanide from solution onto the Au powder (eq 1),  $n_{1s}$  is the saturation coverage ( $\text{mol RNC/g}_{\text{Au}}$ ) of RNC on Au powder,  $[C]$  is the concentration (M or mM) of RNC remaining in solution after contact with the Au powder, and  $S$  is the coverage of RNC on Au powder ( $\text{mol RNC/g}_{\text{Au}}$ ). In this expression, the term  $(n_{1s} - S)$  gives the number of vacant Au binding sites.

Rearrangement of eq 2 produces the familiar form of the Langmuir equation

(eq 3).<sup>26</sup> For a homogeneous adsorbent, a plot of  $[C]/S$  vs.  $[C]$  yields a straight line over the entire concentration range. For a heterogeneous adsorbent,

$$[C]/S = 1/(K_1 n_{1s}) + [C]/n_{1s} \quad (3)$$

curvature should be found in the plot with regions approximating straight lines with different slopes.<sup>27</sup>

Values of  $[C]$  and  $S$  were calculated as described above for samples in which 500 mg of Au were stirred with 1.00 mL solutions (0.60-4.0 mM) of the isocyanide. The linearity of the  $[C]/S$  vs.  $S$  plots demonstrate that type I behavior (according to the classification scheme of Brunauer)<sup>24</sup> is obeyed for all isocyanides studied. Data from a minimum of 5 independent surface studies (at least 30 data points) were used to generate Langmuir isotherm plots for each isocyanide in DCE; plots for  $C_4NC$  and  $C_{18}NC$  are shown in Figure 3. These plots represent Au surface coverages ranging from 70 to 98% of  $n_{1s}$ . Values of  $n_{1s}$  and  $K_1$  (Table 1) were obtained from slopes and intercepts of these plots. Calculated errors for all  $n_{1s}$  and  $K_1$  values in all solvents are reported as standard deviations.

As shown in Table 1, the  $n_{1s}$  and  $n_a$  values agree within experimental error supporting the validity of the Langmuir isotherm treatment. The equilibrium constants,  $K_1$ , also appear to be the same for all RNC in DCE. However, the errors in the  $K_1$  values (Table 1) are large as indicated by the near-zero  $[C]/S$  intercepts in Figure 3. Attempts to determine  $\Delta H_{ads}$  and  $\Delta S_{ads}$  by measuring  $K_1$  for the adsorption of  $C_4H_9NC$  and  $C_{18}H_{37}NC$  from DCE at temperatures ranging from -40 to 40 °C were unsuccessful due to large errors

in the  $K_1$  values. However, it was evident that more isocyanide adsorbed on the Au powder as the temperature was decreased.

**Adsorption of RNC at Low Concentrations.** The Langmuir studies were performed on solutions of relatively high concentrations (0.60 - 4.0 mM) which yielded surface coverages of 70 - 98% of  $n_{1s}$ . When DCE solutions of  $C_4H_9NC$  and  $C_{18}H_{37}NC$  in concentrations of only 0.3 to 0.6 mM were contacted with 500 mg of Au powder *all* of the isocyanides in the 1.00 mL solutions adsorbed to 500 mg Au; this was demonstrated by the absence of a detectable  $\nu(NC)$  band in the DCE solution. These results show that for surface coverages less than approximately 70% of saturation coverage ( $n_{1s}$ ), all of the RNC in solution binds to the Au powder (i.e.,  $[C] = 0.00$  mM). Thus, at coverages less than 70%, RNC binds too strongly to permit the measurement of an equilibrium binding constant  $K_1$ . However, minimum values for  $K_1$  have been estimated for this strongly binding region by using the limit of  $\nu(NC)$  detection (noise level of the spectrophotometer). These estimates give minimum  $K_1$  values of  $1.0 \times 10^6$ . Thus, there are two different adsorption regimes: (a) low coverage ( $< 70\%$ ) where RNC is very strongly adsorbed ( $K_1 > 10^6$ ) and (b) high coverage ( $> 70\%$ ) where RNC is less strongly adsorbed ( $K_1 = 1.0 \times 10^4$  to  $5 \times 10^4$ ). Supporting the existence of these two adsorption regimes are DRIFTS studies of  $C_4H_9NC$  on gold which reveal a decrease of  $\nu(NC)$  from  $2233\text{ cm}^{-1}$  at coverages less than 70%  $n_{1s}$  to  $2225\text{ cm}^{-1}$  at saturation coverage for  $C_4H_9NC$  (Fig. 4). Similar behavior is noted for  $C_{18}H_{37}NC$ , with a decrease from  $2233\text{ cm}^{-1}$  to  $2218\text{ cm}^{-1}$  being observed (Fig. 4).



## Discussion

**DRIFT Spectroscopic Studies of RNC on Au.** DRIFT spectra of RNC on Au powder display a single  $\nu(\text{NC})$  peak for the adsorbed isocyanide. At saturation coverage of the surface, the peak for the bound species occurs at  $2225\text{ cm}^{-1}$  for  $\text{C}_4\text{H}_9\text{NC}$ ,  $\text{C}_6\text{H}_{13}\text{NC}$ ,  $\text{C}_8\text{H}_{17}\text{NC}$ ,  $\text{C}_{12}\text{H}_{25}\text{NC}$  and at  $2218\text{ cm}^{-1}$  for  $\text{C}_{18}\text{H}_{37}\text{NC}$ . This blue shift of approximately  $70\text{ cm}^{-1}$  from that of the free isocyanides ( $2150\text{ cm}^{-1}$ ) is consistent with end-on RNC binding to a single Au atom.<sup>20, 21</sup> This on-top site binding behavior is also observed for CO on Au<sup>28</sup> but contrasts with the well-studied *n*-alkylthiols (RSH) on Au film which reside in three-fold hollows, bridging three Au atoms, as determined by electron diffraction,<sup>29</sup> helium diffraction,<sup>30</sup> and atomic force microscopy (AFM)<sup>12</sup>. This surface adlayer structure corresponds to a 3:1 ratio of surface Au atoms to adsorbed thiol which has been confirmed experimentally for RSH species on gold film.<sup>12, 29, 30</sup> In the present studies, the ratios of surface Au atoms to adsorbed *n*-alkylisocyanides at saturation coverage are 4.8 ( $\text{C}_4\text{H}_9\text{NC}$ ,  $\text{C}_6\text{H}_{13}\text{NC}$ ,  $\text{C}_8\text{H}_{17}\text{NC}$ ), 4.6 ( $\text{C}_{12}\text{H}_{25}\text{NC}$ ), and 4.2 ( $\text{C}_{18}\text{H}_{37}\text{NC}$ ) for isocyanide adsorption from DCE solutions. These ratios are calculated by assuming that the surface of the gold powder has a (111) surface structure, the most thermodynamically stable Au surface. Making use of the measured BET surface area ( $0.33\text{ m}^2/\text{g}$ ) for the gold used in this work gives  $7.6 \times 10^{-6}\text{ mol}$  surface Au atoms per gram of Au powder.<sup>21</sup> Thus, the 4.2 to 4.8 ratio of surface atoms to adsorbed RNC is similar to that observed for CO adsorption ( $5.0$ )<sup>28</sup> on Au film but significantly greater than that ( $3.0$ ) for alkyl thiols. This means that like the analogous adsorption of CO on Au, *n*-alkylisocyanides are less densely packed than SAM's

containing *n*-alkylthiols. This difference may result from different patterns for RNC and RSH adsorption on Au(111) or from different surface structures of Au(111) thin films and powdered Au. Although powdered Au is generally assumed to have a predominantly (111) structure, this has not been established experimentally. The solvent also influences the amount of adsorbed isocyanide (Table 2). Whereas the ratio of surface Au atoms to adsorbed isocyanide is 4.8 ( $C_4H_9NC$ ) and 4.2 ( $C_{18}H_{37}NC$ ) for adsorption from DCE solvent, these ratios decrease to 3.5 ( $C_4H_9NC$ ) and 2.6 ( $C_{18}H_{37}NC$ ) for adsorption from  $MeNO_2$  solvent. As suggested in the Results section, the tighter packing observed when using  $MeNO_2$  may result from the exclusion of more of the polar solvent from the *n*-alkyl region of the adsorbed isocyanides than occurs in the less polar DCE. This allows more isocyanide to adsorb to the surface. Thus, if the assumed (111) surface structure is correct, the ratio of surface Au atoms to adsorbed isocyanide (from nitromethane) is very similar to that observed for thiols on Au film.

**Low Coverage (< 70% of  $n_{111}$ ) Behavior of RNC on Au.** When 500 mg of Au powder is stirred with DCE solutions (1.00 mL) containing RNC concentrations less than 0.6 mM, all of the RNC adsorbs to the surface. The amounts of isocyanide adsorbed on Au under these conditions correspond to surface coverages of 70% or less. As coverage increases beyond 70%, a free RNC peak is observed in the solution after Au contact. Due to the very strong adsorption of RNC when coverage was less than 70%, insufficient RNC remained in solution to be detected which made it impossible to determine  $K_1$  values (eq 1)

for adsorption in this coverage regime. However, a lower limit of  $1.0 \times 10^6$  was estimated (see Results) for  $K_1$  for coverages less than 70% of  $n_{1s}$ .

DRIFT spectroscopic studies of adsorbed  $C_4H_9NC$  and  $C_{18}H_{37}NC$  displayed a single peak at  $2233\text{ cm}^{-1}$  for all detectable coverages less than approximately 70% (Fig. 4). At coverages greater than 70%, the isocyanide peak shifts to lower energy until the surface is essentially saturated at which stage the  $\nu(NC)$  value remains constant. The  $\nu(NC)$  value at saturation occurs at  $2225\text{ cm}^{-1}$  for  $C_4H_9NC$  and at  $2218\text{ cm}^{-1}$  for  $C_{18}H_{37}NC$ . These results indicate that the  $\nu(NC)$  value for  $C_4H_9NC$  and  $C_{18}H_{37}NC$  on Au at coverages less than 70% are higher ( $2233\text{ cm}^{-1}$ ) than for RNC at coverages higher than approximately 70% ( $2225$  or  $2218\text{ cm}^{-1}$ ). In transition metal complexes,<sup>31</sup> high  $\nu(NC)$  values are associated with RNC binding to relatively positive metal centers, which are good  $\sigma$ -electron acceptors from the RNC and poor  $\pi$ -backbonders to the RNC. As applied to the present studies, the higher  $\nu(NC)$  values for the isocyanides at low coverage ( $< 70\%$ ) suggests that these isocyanides are bound to more positive metal centers than isocyanides bound at high coverage ( $> 70\%$ ). At this point, it is not clear whether the low and high coverage regimes represent two types of Au sites or that some reconstruction of the surface occurs at 70% surface saturation.

**High Coverage ( $> 70\%$  of  $n_{1s}$ ) Behavior of RNC on Au.** It was a goal of this study to determine whether an increase in the number of methylene units in the  $n$ -alkyl group of the isocyanide enhances its binding to the gold surface as indicated by an increase in  $K_1$  with increasing chain length. And we also sought to determine the magnitude of this effect. Because RNC binding to the

surface is weaker in the high coverage regime, it was possible to determine equilibrium constants,  $K_1$ , for adsorption to Au powder when solution concentrations gave surface coverages that were greater than 70% of  $n_{1s}$ . The time required to reach equilibrium (Fig. 2) was 24h for  $C_4H_9NC$ ,  $C_6H_{13}NC$ , and  $C_8H_{17}NC$  in DCE. The isocyanide,  $C_{12}H_{25}NC$ , requires a slightly longer settling period (30-36 h) to achieve fully reproducible results. While  $C_{18}H_{37}NC$  gives  $n_{1s}$  and  $n_a$  values that are similar to those observed (Table 1) for the shorter-chain RNC ( $1.5 - 1.6 \times 10^{-6}$  mol/g<sub>Au</sub>) after 24 h, higher coverages resulted after 72 h settling times ( $1.77 \times 10^{-6}$  and  $1.74 \times 10^{-6}$  mol/g<sub>Au</sub>). Figure 2 shows that an isocyanide surface coverage of  $1.5 - 1.6 \times 10^{-6}$  mol/g<sub>Au</sub> occurs at a fairly rapid rate, while binding of additional RNC is much slower and only observed for isocyanides with greater than 11 methylene units in their *n*-alkyl group. Thus, the isocyanides with longer alkyl chains ( $C_{12}H_{25}NC$  and  $C_{18}H_{37}NC$ ) give higher surface coverages ( $n_{1s}$  and  $n_a$ ) but require longer times to establish saturation equilibrium.

Two processes have been observed to be intrinsic to the formation of *n*-alkylthiol SAM's on Au film and both proceed on significantly different time scales.<sup>6, 7, 15, 16</sup> These processes are the initial adsorption of the thiol head group to the Au surface which occurs after seconds of exposure, and the annealing of the *n*-alkyl chains from a less ordered distribution to a predominately all-*trans* conformation after hours to days. It is assumed that isocyanides adsorb to Au in a similar manner. The initial interaction of the  $-N\equiv C$  group represents the fast stage of adsorption which is followed by a slower annealing process in which van der Waals' interactions between the *n*-alkyl chains are optimized.

For the isocyanides with the longest *n*-alkyl chains ( $C_{12}H_{25}NC$  and  $C_{18}H_{37}NC$ ), there is an additional step that is even slower (Fig. 2) and leads to higher coverages on the Au powder; from the solvent dependence (Fig. 2) as noted in the Results section, this very slow process may involve displacement of solvent from the monolayer region by additional isocyanide.

Equilibrium constants,  $K_1$  (Table 1), for the adsorption of isocyanides from DCE solutions onto Au powder fall in the narrow range  $18 \times 10^3$  to  $24 \times 10^3$  for *n*-alkylisocyanides from R = *n*-butyl to *n*-octadecyl. Although  $K_1$  appears to be slightly larger for  $C_{18}H_{37}NC$  than the other isocyanides, the errors associated with the  $K_1$  values are large. However, the more gentle curvature of the adsorption isotherm (Fig. 1) for  $C_4H_9NC$  than  $C_{18}H_{37}NC$  suggests that  $C_{18}H_{37}NC$  binds more strongly. In order to examine further the relative binding abilities of  $C_4H_9NC$  and  $C_{18}H_{37}NC$ , we measured the amounts of these isocyanides that adsorbed when Au powder (500 mg) was stirred with a DCE solution containing both isocyanides. It was necessary to use  $^{13}C$ -labeled  $C_{18}H_{37}N^{13}C$  and unlabeled  $C_4H_9NC$  with  $\nu(NC)$  values of  $2113\text{ cm}^{-1}$  and  $2150\text{ cm}^{-1}$ , respectively, in order to determine their concentrations in solution. The labeled  $C_{18}H_{37}N^{13}C$  was established to have the same extinction coefficient ( $\epsilon = 243 \pm 3\text{ M}^{-1}\text{cm}^{-1}$ ) as  $C_{18}H_{37}NC$  in DCE solution. The usefulness of  $C_{18}H_{37}N^{13}C$  was demonstrated in an experiment in which 1.00 mL of a DCE solution containing 2.0 mM  $C_{18}H_{37}N^{13}C$  and 2.0 mM  $C_{18}H_{37}NC$  was stirred with 500 mg of Au powder and allowed to settle for 3 d. As is evident in Figure 5 (top), the concentrations in solution of both  $C_{18}H_{37}N^{13}C$  and  $C_{18}H_{37}NC$  decrease the same amount after contact with Au, which indicates that equal amounts of both

isocyanides adsorb on the Au as expected. When the same experiment was repeated with 2.0 mM  $C_{18}H_{37}N^{13}C$  and 2.0 mM  $C_4H_9NC$  in DCE solution and 500 mg Au powder, the decrease in concentration of  $C_{18}H_{37}N^{13}C$  was greater than that of  $C_4H_9NC$  (Fig. 5 (bottom)). Using extinction coefficients for their  $\nu(NC)$  absorptions the ratio of  $C_{18}H_{37}N^{13}C/C_4H_9NC$  on the Au powder was calculated to be 4.1. That the system was at equilibrium was demonstrated by experiments in which one isocyanide was first added to the Au surface and then the other was added; in each case the same  $C_{18}H_{37}N^{13}C/C_4H_9NC$  ratio was obtained. The Au powder (500 mg) was first treated with a 2.0 mM DCE solution of one RNC, stirred, allowed to settle for 3 d, and then filtered. This Au powder, already saturated with one isocyanide, was then treated with a 1.00 mL solution containing both  $C_{18}H_{37}N^{13}C$  and  $C_4H_9NC$  in concentrations that provided equal total amounts ( $2.00 \times 10^{-3}$  mmol, both originally on the surface and in the added solution) of the two isocyanides. The mixture was stirred, allowed to settle for 3 d, and the concentrations of the two isocyanides remaining in solution were measured by FTIR. In both experiments, the  $C_{18}H_{37}N^{13}C/C_4H_9NC$  ratio on the Au powder was 4.1, thereby demonstrating that this ratio represents an equilibrium distribution of the two isocyanides. These results also show that both the strongly adsorbed ( $< 70\%$   $n_{1s}$  coverage) and weakly adsorbed ( $>70\%$   $n_{1s}$  coverage) isocyanides achieve equilibrium.

The above  $C_{18}H_{37}N^{13}C - C_4H_9NC$  experiments, as well as the  $K_1$  studies, indicate that  $C_{18}H_{37}NC$  binds more strongly to Au powder than the shorter  $n$ -alkylisocyanides, but the difference is relatively small. As noted in the Introduction, a similar small preference was observed<sup>7</sup> for the long-chain

$C_{22}H_{45}SH$  over  $C_{12}H_{25}SH$ , as indicated by a value of 2.3 for the ratio  $[C_{22}]_{\text{surf}}[C_{12}]_{\text{sol}}/[C_{12}]_{\text{surf}}[C_{22}]_{\text{sol}}$  when the adsorption was performed in isooctane solution; however, it was not established that this system was at equilibrium. On the other hand, a TPD study<sup>17</sup> cited in the Introduction suggests that the difference in van der Waals' forces ( $\sim 11$  kcal/mol) between the *n*-alkyl chains in  $C_{18}H_{37}SH$  and  $C_4H_9SH$  would make  $K_1$  values for the adsorption of  $C_{18}H_{37}SH$  many orders of magnitude larger than those for  $C_4H_9SH$ . It should be noted, however, that the TPD study involves desorption from a SAM on Au(111) into the gas phase. In studies of RSH or RNC adsorption from solution,  $K_1$  values are determined not only by the free energies of adsorption on the surface but also by the free energies of solvation. For a non-polar solvent, the long-chain R group will have a higher solvation energy which will reduce the  $K_1$ ; this would make the difference between the  $K_1$  values for the short- and long-chain *n*-alkyl groups much smaller than predicted by van der Waals' energies alone. The  $K_1$  values and  $C_{18}H_{37}N^{13}C - C_4H_9NC$  results in the present study show that adsorption from DCE solution favors  $C_{18}H_{37}NC$  over  $C_4H_9NC$  by a factor of 4.1 or less. Perhaps this factor would be larger on Au film where SAM formation would be more favorable.

However, the preference for  $C_{18}H_{37}NC$  can be increased by increasing the polarity of the solvent. This is illustrated by the increase in the  $C_{18}H_{37}NC/C_4H_9NC$  ratio of  $K_1$  values (Table 2) from approximately 1.0 in *n*-decane to about 5.3 in the more polar solvent nitromethane. This increase shows that long-chain *n*-alkylisocyanide adsorption is favored by polar

solvents, which have a reduced ability to solvate the long, non-polar *n*-alkyl chains.

### Summary

These studies of *n*-alkylisocyanide adsorption on Au powder establish two adsorption regimes. At surface coverages less than 70% of saturation coverage ( $n_{1s}$  or  $n_s$ ), the equilibrium binding constants,  $K_1$ , are very high ( $> 10^6$ ) and the  $\nu(\text{NC})$  values for the adsorbed isocyanides are relatively high ( $2233 \text{ cm}^{-1}$ ). At surface coverages greater than 70% of  $n_{1s}$ , the  $\nu(\text{NC})$  values are at least  $8 \text{ cm}^{-1}$  lower than those in the low coverage regime, and the  $K_1$  values ( $1.0 \times 10^4 - 5 \times 10^4$ ) are substantially lower than those at low coverage. Measurements of  $K_1$  values in the high coverage regime using DCE solvent show that  $K_1$  values are the same ( $\sim 18 \times 10^3$ ) for *n*-alkylisocyanides ranging from  $\text{C}_4\text{H}_9\text{NC}$  to  $\text{C}_{12}\text{H}_{25}\text{NC}$ , while  $K_1$  ( $24 \times 10^3$ ) appears to be somewhat higher for  $\text{C}_{18}\text{H}_{37}\text{NC}$ . This conclusion is supported by competitive adsorption studies of  $\text{C}_4\text{H}_9\text{NC}$  and  $\text{C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  which show that the  $\text{C}_{18}\text{H}_{37}\text{N}^{13}\text{C}/\text{C}_4\text{H}_9\text{NC}$  ratio of the adsorbed isocyanides is 4.1. In all of these studies, the equilibrium preference for  $\text{C}_{18}\text{H}_{37}\text{NC}$  over  $\text{C}_4\text{H}_9\text{NC}$  is small. The effect of the solvent is to increase the preference for  $\text{C}_{18}\text{H}_{37}\text{NC}$  adsorption with increasing solvent polarity as illustrated by the increase in the  $\text{C}_{18}\text{H}_{37}\text{NC}/\text{C}_4\text{H}_9\text{NC}$  ratio of  $K_1$  values (Table 2) from *n*-decane (1.0) to nitromethane (5.3). Solvents also affect the amount of isocyanide adsorbed at saturation coverage (Table 2); thus, values of  $n_{1s}$  ( $\text{mol RNC}/\text{g}_{\text{Au}}$ ) decrease with the solvent in the order: nitromethane ( $2.82 \times 10^{-6}$ )  $>$  *n*-decane ( $2.44 \times 10^{-6}$ )  $>$  DCE ( $1.77 \times 10^{-6}$ ). These results suggest that some solvents, e.g., nitromethane, are more likely to be excluded from the



hydrocarbon region of the monolayer and replaced by additional *n*-alkylisocyanide.

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Table 1. Values of  $\epsilon$ ,  $n_{1s}$ ,  $n_a$ , and  $K_1$  for Adsorption of RNC on Au from DCE Solvent

	$\epsilon$ ( $M^{-1}cm^{-1}$ )	$n_a^{a, b} \times 10^6$	$n_{1s}^{a, c} \times 10^6$	$K_1 \times 10^{-3}$
C <sub>4</sub> NC	246 $\pm$ 5	1.54 $\pm$ 0.05	1.53 $\pm$ 0.03	18.6 $\pm$ 5.0
C <sub>6</sub> NC	244 $\pm$ 6	1.51 $\pm$ 0.05	1.52 $\pm$ 0.03	17.8 $\pm$ 5.6
C <sub>8</sub> NC	239 $\pm$ 3	1.54 $\pm$ 0.03	1.54 $\pm$ 0.03	18.4 $\pm$ 8.5
C <sub>12</sub> NC	242 $\pm$ 5	1.61 $\pm$ 0.06	1.60 $\pm$ 0.04	18.4 $\pm$ 10.0
C <sub>18</sub> NC	242 $\pm$ 3	1.74 $\pm$ 0.06	1.77 $\pm$ 0.03	24.1 $\pm$ 12.4

<sup>a</sup> mol RNC/ $g_{Au}$ .

<sup>b</sup> Obtained from S vs  $C_{initial}$  plots (Fig. 1).

<sup>c</sup> Calculated from Langmuir isotherm plots (Fig. 3).

Table 2. Values of  $\epsilon$ ,  $n_{1s}$ ,  $n_a$ , and  $K_1$  for Adsorption of  $C_4H_9NC$  and  $C_{18}H_{37}NC$  on Au from *n*-decane, DCE, and  $MeNO_2$  Solvents

	$\epsilon$ ( $M^{-1}cm^{-1}$ )	$n_a^{a, b} \times 10^6$	$n_{1s}^{a, c} \times 10^6$	$K_1 \times 10^{-3}$
<b><math>C_4H_9NC</math></b>				
<i>n</i> -decane	$321 \pm 6$	$1.60 \pm 0.04$	$1.63 \pm 0.04$	$10.1 \pm 7.6$
DCE	$246 \pm 5$	$1.54 \pm 0.03$	$1.54 \pm 0.03$	$18.4 \pm 8.5$
$MeNO_2$	$224 \pm 5$	$2.12 \pm 0.08$	$2.13 \pm 0.06$	$10.0 \pm 2.8$
<b><math>C_{18}H_{37}NC</math></b>				
<i>n</i> -decane	$363 \pm 6$	$2.30 \pm 0.10$	$2.44 \pm 0.05$	$9.9 \pm 3.3$
DCE	$242 \pm 3$	$1.74 \pm 0.06$	$1.77 \pm 0.03$	$24.1 \pm 12.4$
$MeNO_2$	$229 \pm 4$	$2.89 \pm 0.08$	$2.82 \pm 0.06$	$52.5 \pm 16.3$

<sup>a</sup> mol RNC/ $g_{Au}$ .

<sup>b</sup> Obtained from  $S$  vs  $C_{initial}$  plots (Fig. 1).

<sup>c</sup> Calculated from Langmuir isotherm plots (Fig. 3).

Figure 1. Plots of coverage  $S$  (mol RNC/g<sub>Au</sub>  $\times 10^6$ ) versus  $C_{\text{initial}}$  (mM) for adsorption of  $C_4H_9NC$  and  $C_{18}H_{37}NC$  on Au from DCE solvent.

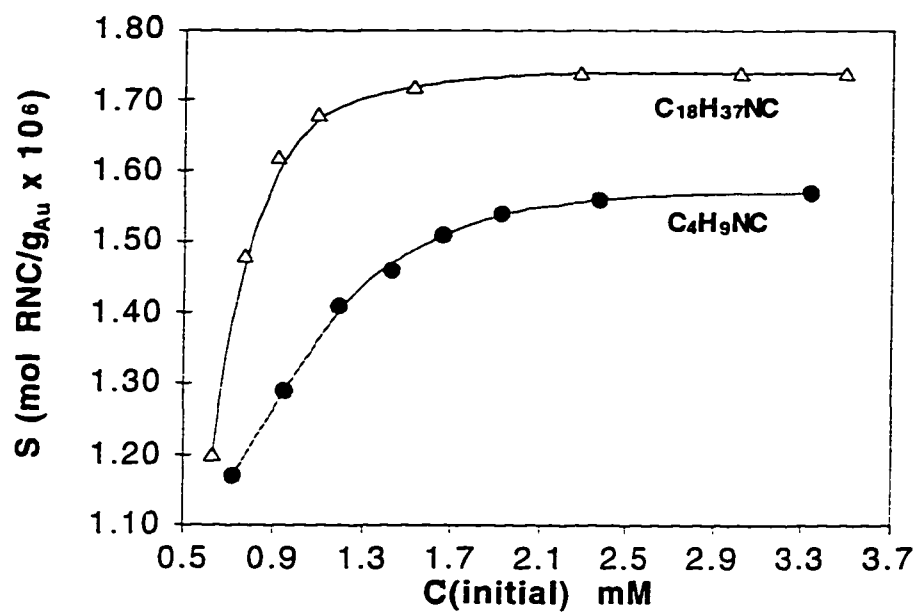


Figure 2. Plots of coverage  $S$  ( $\text{mol RNC/g}_{\text{Au}} \times 10^6$ ) versus time (h) for adsorption of  $\text{C}_4\text{H}_9\text{NC}$  (top) and  $\text{C}_{18}\text{H}_{37}\text{NC}$  (bottom) on Au from three solvents.

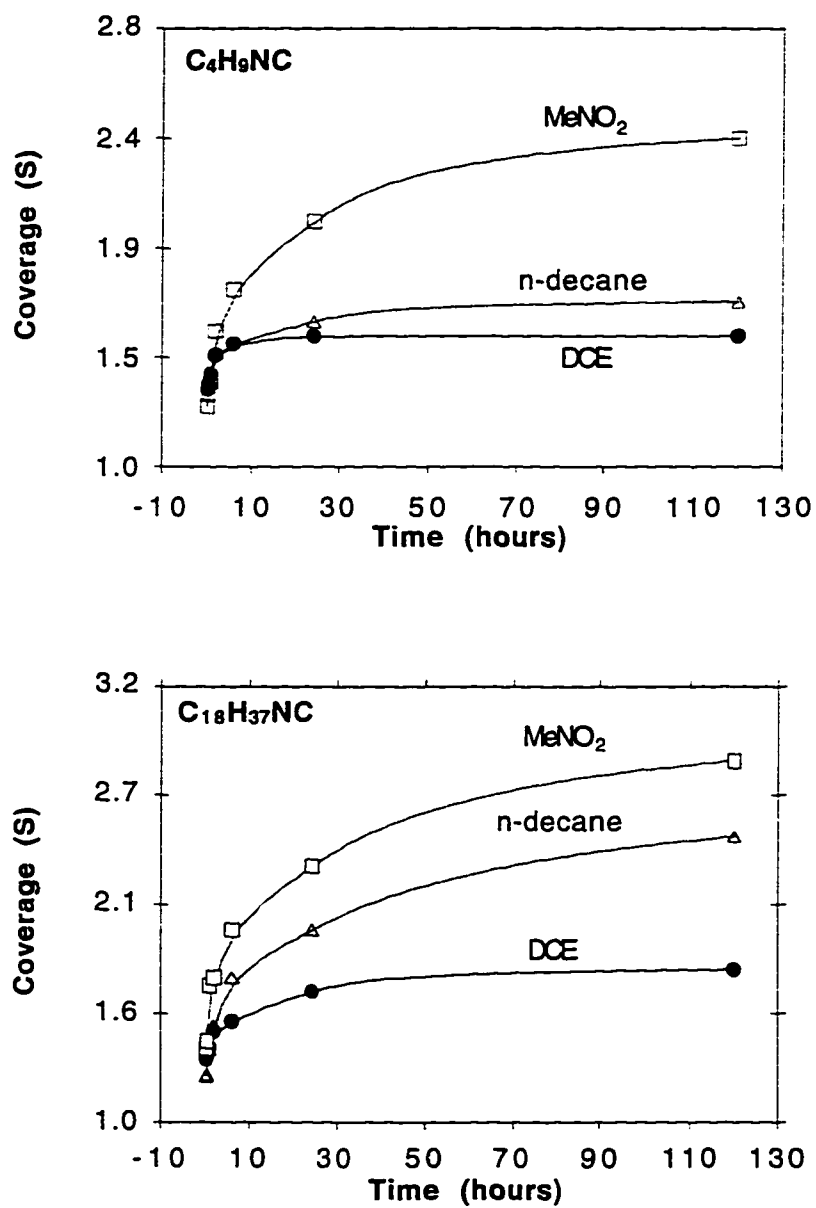




Figure 3. Langmuir isotherm plots of  $[C]/S$  ( $(\text{mM} \cdot \text{g}_{\text{Au}})/\text{mol}$ ) versus  $[C]$  (mM) for  $\text{C}_4\text{H}_9\text{NC}$  (top) and  $\text{C}_{18}\text{H}_{37}\text{NC}$  (bottom) in DCE.

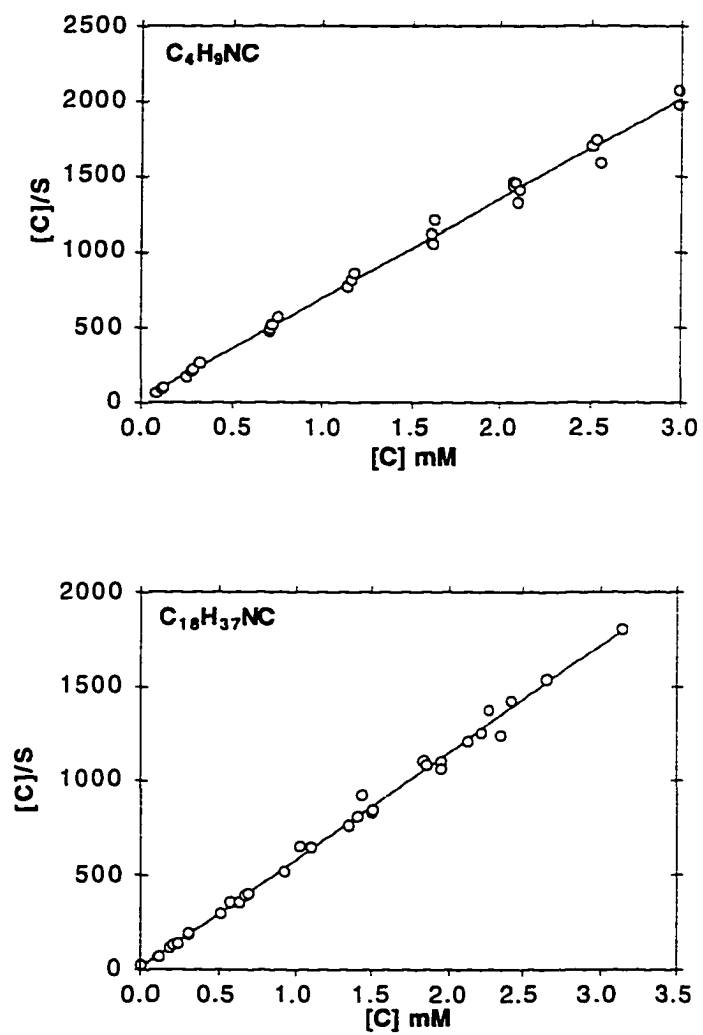


Figure 4. Plots of  $\nu(\text{NC})$  and coverage (as  $\%n_{1s}$ ) versus  $C_{\text{initial}}$  for  $\text{C}_4\text{H}_9\text{NC}$  (top) and  $\text{C}_{18}\text{H}_{37}\text{NC}$  (bottom) in DCE.

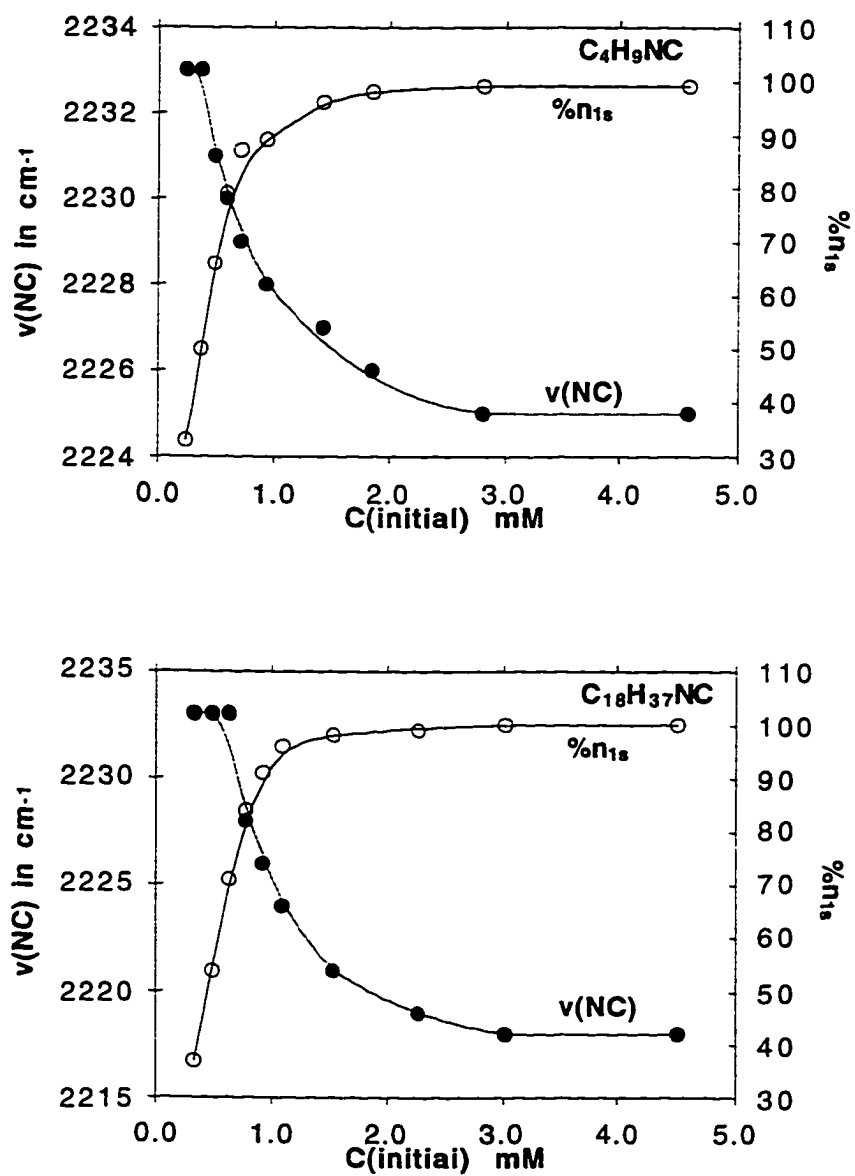
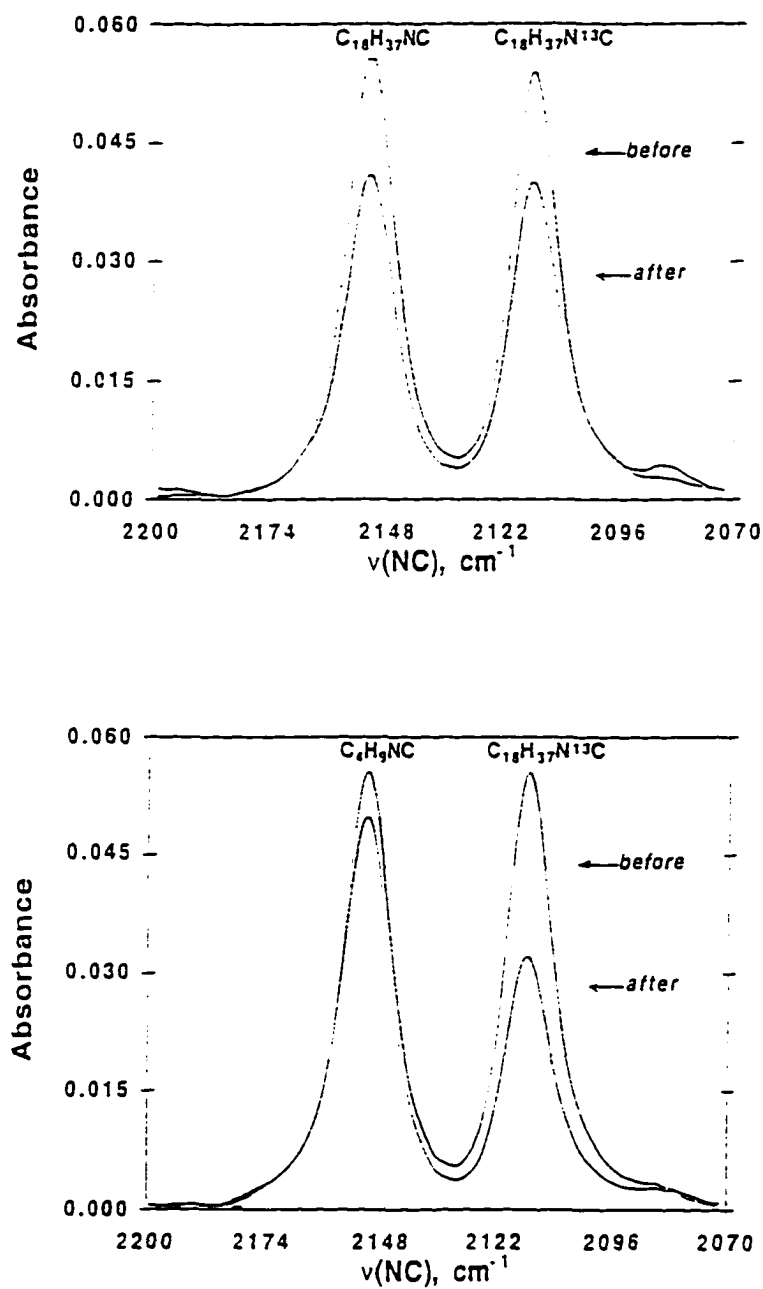


Figure 5. Solution FT-IR spectra of equimolar  $C_{18}H_{37}NC$  and  $C_{18}H_{37}N^{13}C$  in DCE before and after contact with Au powder (top) and equimolar  $C_4H_9NC$  and  $C_{18}H_{37}N^{13}C$  in DCE before and after contact with Au powder (bottom).



# KINETIC AND EQUILIBRIUM STUDIES OF THE ADSORPTION OF BI- AND TRIDENTATE ISOCYANIDES ON GOLD POWDER

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## Abstract

DRIFTS studies of diisocyanides ( $\text{C}\equiv\text{N}-(\text{CH}_2)_x-\text{N}\equiv\text{C}$ , where  $x = 2, 4, 6, 8$ , and  $12$ ; *m*- and *p*-xylyl( $\text{NC}$ )<sub>2</sub>, xylyl =  $-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$ ) and triisocyanides (1,1,1-tris(isocyanomethyl)ethane (Tripod( $\text{NC}$ )<sub>3</sub>) and tris[2-isocyanoethyl]amine (Tren( $\text{NC}$ )<sub>3</sub>)) adsorbed on Au powder show that all of their -NC groups are coordinated to the surface. The  $\nu(\text{NC})$  values ( $\text{cm}^{-1}$ ) for all of the adsorbed ligands are  $\sim 2150 \text{ cm}^{-1}$  which indicates that each of the -NC groups is bound through the carbon to a single Au atom. The saturation coverages ( $n_{1s}$ ) for the diisocyanides decrease as the linking  $-(\text{CH}_2)_x-$  group lengthens from  $x = 2$  to  $x = 12$ . At saturation coverage, the number of moles of  $-\text{N}\equiv\text{C}$  groups coordinated for  $\text{C}_{12}(\text{NC})_2$  is similar to that for the monoisocyanide  $n\text{-C}_{18}\text{H}_{37}\text{NC}$ , while twice as many -NC groups are adsorbed for  $\text{C}_2(\text{NC})_2$  than  $n\text{-C}_{18}\text{H}_{37}\text{NC}$ . Qualitative kinetic measurements show that all of the monoisocyanide,  $n\text{-C}_{18}\text{H}_{37}\text{NC}$ , adsorbed on Au powder is displaced by  $\text{C}_4(\text{NC})_2$  within 90 min. However, only 39% of the diisocyanide *m*-xylyl( $\text{N}^{13}\text{C}$ )<sub>2</sub> is displaced by  $\text{C}_4(\text{NC})_2$  even after 120 h demonstrating that only 34-39% of the diisocyanide *m*-xylyl( $\text{N}^{13}\text{C}$ )<sub>2</sub> is exchangeable while the remaining 61-66% of the diisocyanide is kinetically inert to exchange. The existence of two adsorption regimes, low

coverage (61-66%) and high coverage (above 61-66%), on the Au powder is supported by a variety of evidence. Pseudo-equilibrium constants ( $Q_{ab}$ ), which probably include both kinetic and thermodynamic factors, for the adsorption of diisocyanides on Au increase significantly as the  $-(CH_2)_x-$  link between the -NC groups becomes shorter. The  $C_2(NC)_2$  ligand has the highest binding affinity ( $Q_{ab}$ ). These studies also show that the relative binding affinities of the isocyanides increase as the number of -NC groups in the ligand increases ( $RNC < R(NC)_2 < R(NC)_3$ ).

### Introduction

Understanding the factors which influence the stability of self-assembled monolayers (SAM's) on metal surfaces is necessary if these systems are to be employed in practical applications. Toward achieving this goal, numerous studies of the chemisorption of *n*-alkyl- and arylthiols (RSH) on gold surfaces have been reported.<sup>1-4</sup> It has been observed that the structure of the aryl or alkyl group in the thiol influences the stability of the self-assembled monolayers.<sup>5,6</sup> In principle, the stability of a SAM could be enhanced by introducing more than one -SH group into the adsorbate which would lead to multiple points of attachment on the Au surface. However, reports of multi-thiol ligand adsorption on Au surfaces have involved either a polymer that has been functionalized with thiol side chains<sup>7</sup> or a rigid dithiol in which it is possible for only one sulfur atom to attach to the surface.<sup>8-10</sup> To date the thermodynamic stability afforded by multiple points of attachment has yet to be determined.

As surface adsorbates, isocyanides ( $\text{R-N}\equiv\text{C}$ ) have a very different surface-binding head group than their well studied thiolate counterparts. Results from this group<sup>11-13</sup> have demonstrated that, like the organosulfur systems, modifications of the alkyl or aryl R group affect the surface coverage and stability of the resulting isocyanide monolayer on Au powder. In addition, studies of *n*-alkylisocyanide adsorption from 1,2-dichloroethane (DCE) solution on Au powder have shown that two distinct regimes exist for the chemisorption of RNC on Au.<sup>13</sup> At surface coverages less than approximately 70% of saturation coverage ( $n_{1s}$ ), the equilibrium binding constants,  $K_1$  (eq 1),



are very high ( $> 10^6$ ) and the  $\nu(\text{NC})$  values ( $2233 \text{ cm}^{-1}$ ) for the adsorbed isocyanides are also higher than those observed at coverages greater than 70% of  $n_{1s}$ . At the higher surface coverages, the  $\nu(\text{NC})$  values are at least  $8 \text{ cm}^{-1}$  lower than those in the low coverage regime, and the measured  $K_1$  values ( $1.8 \times 10^4 - 2.4 \times 10^4$ ) are substantially lower.

Despite their excellent ligation properties, few studies of the binding of bi- and tridentate isocyanide ligands in coordination complexes,<sup>14</sup> and even fewer describing their adsorption on metal surfaces,<sup>10, 11</sup> have been reported. Most notable of these is a report<sup>10</sup> in which it was discovered that diisocyanides with flexible backbones such as  $\text{C}\equiv\text{N}-(\text{CH}_2)_6-\text{N}\equiv\text{C}$  and  $\text{C}\equiv\text{N}-(\text{CH}_2)_{12}-\text{N}\equiv\text{C}$  bind to Au film through both  $-\text{N}\equiv\text{C}$  groups. It was determined using ellipsometry that a SAM formed by the adsorption of a diisocyanide with a flexible polymethylene link between the  $-\text{N}\equiv\text{C}$  groups produced a smaller measured ellipsometric thickness than a diisocyanide with an inflexible backbone such as

1,4-phenylenediisocyanide. This report, however, focused on the utility of diisocyanides as tethers for the attachment of gold and nickel cluster complexes to a Au film surface.

The present report describes Au powder chemisorption studies of a series of polymethylene ( $\text{CH}_2$ )<sub>x</sub> and xylylene ( $-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-$ )-linked diisocyanides, as well as two tripodal triisocyanides (Chart 1). All isocyanide species studied were designed with the intention that adsorption to the Au surface could occur through all available isocyanide ( $-\text{N}\equiv\text{C}$ ) groups. Solution and surface (DRIFT) FTIR measurements of the relative surface binding affinities of these isocyanides were conducted by competing two isocyanides (one  $^{13}\text{C}$ -labeled) for the Au powder surface. Also, amounts of the isocyanides adsorbed at saturation coverage were determined for the range of di- and tri-isocyanide structures. And qualitative rates of exchange of adsorbed isocyanides in the low and high coverage regimes were measured.

### Experimental Section

**General Procedure.** All manipulations were performed in air unless otherwise stated. All solvents including 1,2-dichloroethane (DCE) were reagent or HPLC grade and used as purchased. The reagents ethylenediamine, 1,4-butanediamine, 1,8-octanediamine, *m*- and *p*-xylylenediamine, tris(2-aminoethyl)amine, 1,1,1-tris(hydroxyethyl)ethane, benzenesulfonyl chloride, sodium azide, lithium aluminum hydride and benzyltriethylammonium chloride were purchased from Aldrich and used as received. Purchased hexamethylenediisocyanide (Aldrich) was vacuum-distilled and checked for purity ( $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR and FTIR) prior to use.

The Au powder for this work was prepared<sup>11</sup> and cleaned as described previously.<sup>13</sup> Routine BET surface area measurements of the Au powder were performed on a Micromeritics AccuSorb 2100E instrument using Kr as the adsorbing gas at 77 K. The measured surface area of the Au powder used in these studies was  $0.29 \pm 0.03 \text{ m}^2/\text{g}$ .

The  $^1\text{H}$  NMR spectra were obtained on samples in  $\text{CDCl}_3$  solvent using a Nicolet-NT 300 MHz spectrometer with TMS as the internal reference ( $\delta=0.00$  ppm). The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were obtained on samples in  $\text{CDCl}_3$  solvent using a Varian VXR-300 MHz spectrometer with  $\text{CDCl}_3$  as the internal standard ( $\delta=77.06$  ppm). All infrared spectra were recorded on a Nicolet 560 spectrophotometer equipped with a TGS detector in the main compartment and an MCT detector in the auxiliary experiment module (AEM). The AEM housed a Harrick diffuse reflectance accessory. All solution FTIR spectra were recorded using a NaCl cell (1.0 mm) in the main compartment with the instrument set for  $4 \text{ cm}^{-1}$  resolution and 128 scans. All DRIFT spectra, using 512 scans and  $4 \text{ cm}^{-1}$  resolution, were recorded on samples in the Harrick microsampling cup. The background spectrum used for the DRIFT spectra was taken on clean gold powder. Spectra were routinely baseline and purge corrected.

**Synthesis of di- and triisocyanides ( $\text{R}(\text{NC})_2$  and  $\text{R}(\text{NC})_3$ ).** The triisocyanide, 1,1,1-tris(isocyanomethyl)ethane ( $\text{Tripod}(\text{NC})_3$ ) was synthesized as described previously.<sup>15</sup> The compounds 1,2-diisocynoethane ( $\text{C}_2(\text{NC})_2$ ), 1,4-diisocyanobutane ( $\text{C}_4(\text{NC})_2$ ), 1,8-diisocyanooctane ( $\text{C}_8(\text{NC})_2$ ),



1,12-diisocyanododecane ( $C_{12}(NC)_2$ ), *m*-xylylenediisocyanide (*m*-xylyl( $NC$ )<sub>2</sub>), *p*-xylylenediisocyanide (*p*-xylyl( $NC$ )<sub>2</sub>), and tris(2-isocyanoethyl)amine (Tren( $NC$ )<sub>3</sub>) were synthesized from the di- and triamines (10 mmol) using a slightly modified version of that previously described.<sup>10</sup> The following describes the alterations made to the published route: After separation and drying of the organic phase over  $K_2CO_3$ , the volatiles were removed from the organic layer under vacuum. The resulting oil (usually orange/brown) was then dissolved in 25 mL of  $CH_2Cl_2$  (dried with  $CaH_2$ ) and chromatographed using  $CH_2Cl_2$  on a 2 x 10 cm silica column (40 mm silica particle size, Scientific Adsorbents Inc.). Fractions from the column were monitored by FTIR spectroscopy for isocyanide ( $\nu(NC) = 2150\text{ cm}^{-1}$  in  $CH_2Cl_2$ ) and collected upon detection. Removal of solvent under vacuum at 25°C produced spectroscopically ( $^1H$  and  $^{13}C\{^1H\}$  NMR and FTIR) pure isocyanides in low to moderate yields (30-60%). The synthesized diisocyanides were isolated as colorless liquids or solids at room temperature and their spectroscopic data matched those that were previously reported for  $C_2(NC)_2$ ,<sup>16</sup>  $C_4(NC)_2$  and  $C_8(NC)_2$ ,<sup>17</sup>  $C_{12}(NC)_2$ ,<sup>10</sup> and *m*- and *p*-xylyl( $NC$ )<sub>2</sub>.<sup>18</sup> The  $^{13}C$ -labeled *m*-xylylenediisocyanide (*m*-xylyl( $N^{13}C$ )<sub>2</sub>) and 1,12-diisocyanododecane ( $C_{12}(N^{13}C)_2$ ) used in the competitive binding studies was prepared using the same procedure as that used for the nonlabeled diisocyanides, except  $^{13}CHCl_3$  (Cambridge Isotopes Inc.) was substituted for  $CHCl_3$  as the dichlorocarbene source.

**Tris[2-isocyanoethyl]amine (Tren(NC)<sub>3</sub>).** 33% yield. IR (DCE):  $\nu(\text{NC}) = 2150 \text{ cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  3.50 (s, 2H,  $\alpha\text{-CH}_2$ ), 3.00 (s, 2H,  $\beta\text{-CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  158.0 (t,  $J_{\text{CN}}=5.5 \text{ Hz}$ , -NC), 53.8 (s, 2H,  $\beta\text{-CH}_2$ ), 41.0 (t,  $J_{\text{CN}}=6.3 \text{ Hz}$ ,  $\alpha\text{-CH}_2$ ). MS:  $m/z$  177 (M+H).

**DRIFT Analysis of Di- and Triisocyanides on Au Powder.** All DRIFTS data were obtained on 200 mg of Au powder which was treated with a 1.0 mM DCE solution of the desired di- or triisocyanide in a 16 mm Pyrex test-tube. The sample was then capped tightly with a teflon-lined screw-cap, shaken for 30 s on a Vortex Genie 2 mixer (Fisher) and allowed to settle at room temperature. The Au powder from each sample was then filtered from the remaining solution using a Buchner funnel and filter paper. Exactly 50 mg of the dry Au powder was then introduced through a micro funnel into a microsampling cup for DRIFT analysis.

**Langmuir Isotherm Studies of Di- and Triisocyanides on Au Powder.** Stock solutions (approximately 20 mM) of each isocyanide ligand were made by diluting a weighed amount of the compound to 25.00 mL in a volumetric flask with 1,2-dichloroethane (DCE) solvent. Extinction coefficients ( $\epsilon$  in  $\text{M}^{-1} \text{ cm}^{-1}$ , Table 1) of the  $\nu(\text{NC})$  band were obtained for the compounds from Beer-Lambert plots. Other solution concentrations were prepared by serial dilution of the 20 mM stock solution. A 1.00 mL aliquot of the desired isocyanide concentration (ranging from 0.5 to 3.0 mM) was added to a 16 mm Pyrex test tube containing 500 mg of clean Au powder. The sample tube was then capped tightly with a teflon-lined screw-cap, shaken for 30 s, and allowed to settle undisturbed. After 24 h, a sample of the solution over the gold powder was

withdrawn from each tube by syringe. The concentration of the mono-, di-, or triisocyanide in the separated liquid was determined by FTIR spectroscopy using the  $\nu(\text{NC})$  band intensity. A typical series of measurements for the Langmuir isotherm plots required 8 to 14 solutions which were each analyzed as described above. All procedures were performed at room temperature and are similar to those previously reported for the adsorption of monoisocyanides on Au.<sup>13</sup>

**Relative Binding Affinity ( $Q_{\text{ab}}$ ) Studies.** Since all of the isocyanides exhibit  $\nu(\text{NC})$  absorptions (Table 1) at  $\sim 2150 \text{ cm}^{-1}$ , it was necessary to prepare  $^{13}\text{C}$  analogs of  $n\text{-C}_{18}\text{H}_{37}\text{NC}$ ,  $^{13}\text{C}_{12}(\text{NC})_2$ , and  $m\text{-xylyl}(\text{NC})_2$  in order to determine concentrations of these isocyanides and unlabeled competing isocyanides remaining in solution after contact with Au powder; the  $^{13}\text{C}$ -labeled isocyanides showed a  $\nu(\text{NC})$  absorption at  $\sim 2113 \text{ cm}^{-1}$  (Table 1). For the competitive binding studies, the  $^{13}\text{C}$ -labeled isocyanide was  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  (for  $n\text{-C}_4\text{H}_9\text{NC}$ ),  $\text{C}_{12}(\text{N}^{13}\text{C})_2$  (for  $n\text{-C}_{18}\text{H}_{37}\text{NC}$ ), or  $m\text{-xylyl}(\text{N}^{13}\text{C})_2$  (all other di- and triisocyanides). A 1.00 mL aliquot of a DCE solution containing the desired concentrations of both isocyanides was added to a 16 mm Pyrex test tube containing 200 mg of clean Au powder. The sample tube was then capped tightly with a teflon-lined screw-cap, shaken for 30 s and allowed to settle undisturbed. After at least 12 h of settling, a sample of the solution over the gold powder was withdrawn by syringe. Time-dependent studies (see next section) showed that steady-state concentrations of the isocyanide in solution and on the surface were achieved within 4 h; 12 h settling periods ensured the attainment of a steady-state. The solution was analyzed for concentrations of

the two competing isocyanides ( $[C_a]$  and  $[C_b]$ ). The remaining solution was then removed from the Au powder by filtration and the powder was analyzed by DRIFTS. The ratio ( $S_a/S_b$ ) of the amounts of two diisocyanides on the Au powder was simply the ratio of their absorption intensities (DRIFTS) in the  $\nu(\text{NC})$  region, which were adjusted for their different extinction coefficients (Table 1). For competition studies involving di- and triisocyanides, the intensity of the triisocyanide band was multiplied by 0.67; for studies of mono- and diisocyanides, the absorbance of the monoisocyanides was multiplied by 2.0. This method of calculating  $S_a/S_b$  assumes that the extinction coefficients of the isocyanides are the same as they are in solution (Table 1). That this assumption is valid is supported by the results of competition studies between  $n\text{-C}_{18}\text{H}_{37}\text{NC}$  and  $\text{C}_{12}(\text{N}^{13}\text{C})_2$  and between  $\text{C}_6(\text{NC})_2$  and  $m\text{-xylyl}(\text{N}^{13}\text{C})_2$  which gave the same  $S_a/S_b$  ratios by both the DRIFT method and by measuring the solution concentrations of the isocyanides. The solution measurement method gave large errors when relatively high isocyanide solution concentrations were used or when it was necessary to use a significantly higher concentration of one of the competing isocyanides. Calculation of the relative binding affinities ( $Q_{ab}$ ) are described in the Results.

**Time Dependent Competition Studies.** For studies in which both isocyanides were added simultaneously to the Au powder (as in the  $Q_{ab}$  studies) a 1.0 mL aliquot of a solution containing the desired concentrations of both competitors was added to a series of 16 mm Pyrex test tubes, each containing 200 mg of clean Au powder. Each sample tube was capped tightly with a teflon-lined screw-cap, shaken for 30 s and allowed to settle undisturbed. After a specific

settling time, the solution over the gold powder was analyzed for the concentrations of the two isocyanides, and the Au powder was separated by filtration with a Buchner funnel and analyzed by DRIFTS.

For studies involving sequential addition of the isocyanides to the Au, a 16 mm Pyrex test tube containing 200 mg of Au powder was treated with a 1.0 mL aliquot of a 1.0 mM (diisocyanide) or 2.0 mM (monoisocyanide) solution of the first isocyanide. This sample tube was then capped tightly with a teflon-lined screw-cap, shaken for 30 s and allowed to settle undisturbed for at least 12 h. The powder was then filtered using a Buchner funnel and filter paper and analyzed by DRIFTS to ensure that the surface was covered by the isocyanide. Absence of a  $\nu(\text{NC})$  absorption at  $2150\text{ cm}^{-1}$  verified that no physisorbed isocyanide was present on the powder. This 200 mg sample of Au was then treated with a 1.00 mL aliquot of a DCE solution that contained the appropriate concentration of the competing isocyanide (i.e., the isocyanide not already present on the Au surface) and a concentration of the first isocyanide  $[1.0\text{ mM} - (1000\text{ mM/M} \times ((0.200\text{ g}_{\text{Au}} \times n_{1s})/(0.00100\text{ L}))]$  (where  $n_{1s}$  is the saturation coverage in  $\text{mol R}(\text{NC})_2/\text{g}_{\text{Au}}$  as determined by the Langmuir isotherm technique in Table 2) that would make the total amounts (in solution and on the Au surface) of the two isocyanides equal (1.0 mM). In competition studies of the monoisocyanide  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  and the diisocyanide  $\text{C}_4(\text{NC})_2$ , total concentrations of  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  and  $\text{C}_4(\text{NC})_2$  were 2.0 mM and 1.0 mM, respectively. The sample tube was then capped tightly with a teflon-lined screw-cap, shaken for 30 s and allowed to settle undisturbed for a specific length of time. The powder was then filtered using a Buchner funnel and

filter paper and analyzed by DRIFTS to determine the relative amounts of the two isocyanides on the surface. A series of samples was prepared and analyzed in the same manner at different times after treatment with the solution of the second isocyanide.

## Results

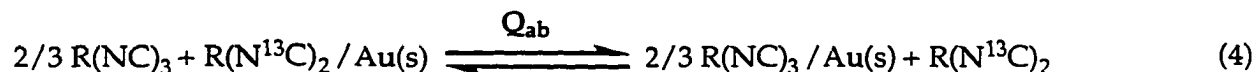
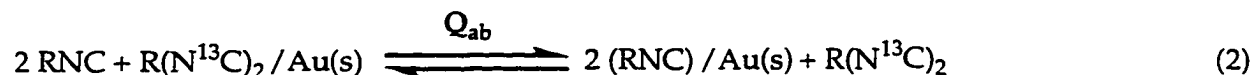
**Solution Concentration Measurements.** Extinction coefficients (Table 1) from Beer-Lambert plots of  $\nu(\text{NC})$  absorbances versus known isocyanide solution concentrations (0.10 - 10.0 mM) were reproducible over the course of these studies and were used to determine the initial concentrations  $C_{\text{initial}}$  and the concentrations  $[C]$  (mM) of isocyanide remaining in solution after stirring with Au powder. The amount of RNC adsorbed on the Au surface,  $S$  (mol RNC/g<sub>Au</sub>), was calculated as the amount of RNC lost from 1.00 mL of solution,  $[(C_{\text{initial}} - [C]) \times 1.00 \text{ mL}]/10^6$ , per g of Au powder used.

**DRIFT Spectroscopic Studies of the Isocyanides on Au Powder.** DRIFT spectra of Au powder treated with DCE solutions of di- and triisocyanides show a single broad ( $\sim 30 \text{ cm}^{-1}$  width at half-height)  $\nu(\text{NC})$  absorption for all species studied (Table 1). The  $\nu(\text{NC})$  value of the surface bound isocyanide is shifted to higher energy (about  $70 \text{ cm}^{-1}$ ) from that of the free di- and triisocyanides in solution. There is no  $\nu(\text{NC})$  absorption ( $2150 \text{ cm}^{-1}$ ) corresponding to unbound  $-\text{N}\equiv\text{C}$  groups. Thus, all  $-\text{N}\equiv\text{C}$  groups are chemically bonded to the Au surface. The similarity of the  $\nu(\text{NC})$  value to that of monoisocyanides (RNC) on Au powder<sup>12, 13</sup> suggests that each isocyanide carbon is adsorbed on one Au atom. The  $\nu(\text{NC})$  values decrease with surface coverage of the di- and triisocyanides from  $\sim 2235 \text{ cm}^{-1}$  at coverages less than 70% of saturation coverage to the values

listed in Table 1 at saturation coverage. This dependence of  $\nu(\text{NC})$  on coverage was studied in detail for the adsorption of *n*-alkylisocyanides on Au powder.<sup>13</sup>

**Determination of Saturation Coverage ( $n_{1s}$ ).** Attempts to determine equilibrium binding constants,  $K_1$ , for the di- and triisocyanides using Langmuir isotherm plots,  $[C]/S$  vs.  $[C]$ , as was done for the mono-isocyanides,<sup>12, 13</sup> were unsuccessful due to the strong binding affinities of the polyisocyanides for the Au powder. This resulted in plots with near-zero intercepts and large errors. However, the slopes of these plots gave consistent values for the amount of isocyanide adsorbed at saturation coverage ( $n_{1s}$ , mol of isocyanide ligand/ $g_{\text{Au}}$ ) (Table 2).

**Determination of Relative Affinities ( $Q_{ab}$ ) of Isocyanides for Au Powder.** In order to determine relative affinities of the mono-, di-, and triisocyanides for Au powder, we measured (see Experimental) the amounts of the isocyanides adsorbed when a mixture of two isocyanides in DCE solution was added to clean Au powder at room temperature. The relative affinities of the two isocyanide ligands are expressed as measured  $Q_{ab}$  values for the pseudo-equilibria involving competition of mono- and diisocyanides (eq 2), two



diisocyanides (eq 3), and di- and triisocyanides (eq 4). The measured  $Q_{ab}$  values (eqs 5-7) are probably not equilibrium constants because it is likely that the amounts of the two isocyanides on the surface are determined by both thermodynamic and kinetic factors as described in the next section. In eq 5-7,

$$Q_{ab} = S_a[C]_b/S_b[C]_a^2 \quad (5)$$

$$Q_{ab} = S_a[C]_b/S_b[C]_a \quad (6)$$

$$Q_{ab} = S_a[C]_b/S_b[C]_a^{2/3} \quad (7)$$

$[C]_a$  is the concentration (mM) of the unlabeled isocyanide in solution and  $S_a$  is the amount adsorbed on Au, while  $[C]_b$  is the concentration (mM) of  $RN^{13}C$  or  $R(N^{13}C)_2$  in solution after Au contact, and  $S_b$  is the amount of adsorbed  $RN^{13}C$  or  $R(N^{13}C)_2$  on the Au. The measured  $Q_{ab}$  values (Table 3) have been normalized to *m*-xylyl(NC)<sub>2</sub> ( $Q_{ab} = 1.0$ ) to give relative  $Q_{ab}$  values for all isocyanides studied. For isocyanides whose reactions could not be measured directly, the relative  $Q_{ab}$  values were obtained by multiplying appropriate measured  $Q_{ab}$  values. For example, the relative  $Q_{ab}$  value for *n*-C<sub>18</sub>H<sub>37</sub>NC (0.0017) was calculated by multiplying measured  $Q_{ab}$  values for the *n*-C<sub>18</sub>H<sub>37</sub>NC/C<sub>12</sub>(N<sup>13</sup>C)<sub>2</sub> (0.076) and C<sub>12</sub>(NC)<sub>2</sub>/*m*-xylyl(N<sup>13</sup>C)<sub>2</sub> (0.022) reactions.

**Kinetic Effects on the Competitive Adsorption of Two Isocyanides.** The measured  $Q_{ab}$  values for the mono-, di-, and triisocyanides in Table 3 were determined using solutions with varying concentrations of the competing isocyanides. That these are not equilibrium constants is shown by competitive adsorption studies in which DCE solutions containing 1.0 mM *m*-xylyl(N<sup>13</sup>C)<sub>2</sub> and increasing concentrations of C<sub>6</sub>(NC)<sub>2</sub> were contacted with clean Au



powder (Table 4). Instead of remaining constant, the measured  $Q_{ab}$  values decrease modestly as the concentration of  $C_6(NC)_2$  increases which means that more  $m$ -xylyl( $N^{13}C$ )<sub>2</sub> than  $C_6(NC)_2$  adsorbs at the higher concentrations of  $C_6(NC)_2$  than is expected for a system at equilibrium.

In order to understand the role that kinetics may play in these changes in  $Q_{ab}$  two competition experiments were conducted in order to determine whether reversible exchange occurs between an isocyanide adsorbed on the Au and an isocyanide in solution. In the first study, 200 mg of Au powder was treated with a 1.0 mM solution of one of the isocyanides,  $m$ -xylyl( $N^{13}C$ )<sub>2</sub> or  $m$ -xylyl(NC)<sub>2</sub>. The Au (with saturation coverage of the first isocyanide) was filtered and subsequently treated with a solution containing both  $m$ -xylyl( $N^{13}C$ )<sub>2</sub> and  $m$ -xylyl(NC)<sub>2</sub> in concentrations such that both isocyanides are present in the system (solution + surface = 1.0 mM in 1.0 mL solution) in equimolar amounts (see Experimental). DRIFTS spectra of the Au powder show how the relative amounts of these isocyanides on the surface change with time. As seen in the uppermost curve in Figure 1, only 34% of the initially adsorbed  $m$ -xylyl( $N^{13}C$ )<sub>2</sub> is displaced by  $m$ -xylyl(NC)<sub>2</sub> even after 120 h of contact with the Au; the expected 1:1 ratio of these isocyanides is not achieved under these conditions. Similarly, about 34% of the initially adsorbed  $m$ -xylyl(NC)<sub>2</sub> is displaced relatively rapidly (lowermost curve in Figure 1) from the Au by  $m$ -xylyl( $N^{13}C$ )<sub>2</sub> but the expected 1:1 ratio is not achieved even after many hours. The 1:1 ratio is achieved, however, when an equimolar solution of the two isocyanides is contacted with clean Au powder (middle line in Figure 1). From these experiments, it is evident that approximately 34% of

adsorbed isocyanide is readily displaced. Thus, whichever isocyanide adsorbs to the Au initially can be only partially (~ 34%) displaced.

In the second series of experiments (Fig. 2), two different isocyanides, *m*-xylyl(N<sup>13</sup>C)<sub>2</sub> and C<sub>4</sub>(NC)<sub>2</sub>, with similar Q<sub>ab</sub> values were studied in the same way. When *m*-xylyl(N<sup>13</sup>C)<sub>2</sub> was on the surface initially, only 39% of it was displaced by C<sub>4</sub>(NC)<sub>2</sub>. When C<sub>4</sub>(NC)<sub>2</sub> was initially on the Au, only 36% of it was displaced. These two experiments establish that only 34-39% of the adsorbed isocyanide is displaced by another isocyanide under these conditions. When an equimolar solution (1.0 mM of each in 1.0 mL of DCE) of these isocyanides is contacted with clean Au powder, C<sub>4</sub>(NC)<sub>2</sub> initially predominates on the surface (middle curve in Fig. 2), but with time an approximately 1:1 ratio is achieved, as expected from their Q<sub>ab</sub> values. The Q<sub>ab</sub> value may not be an equilibrium distribution of the two isocyanides on the surface because if one of the isocyanides, e.g. C<sub>4</sub>(NC)<sub>2</sub> in this case, adsorbs more rapidly than the other, only part (36-39%) of the adsorbed isocyanide can exchange rapidly enough with the other isocyanide in solution to achieve equilibrium.

For comparison with the above *m*-xylyl(N<sup>13</sup>C)<sub>2</sub>/C<sub>4</sub>(NC)<sub>2</sub> studies, the competitive adsorption of the monoisocyanide, *n*-C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C and C<sub>4</sub>(NC)<sub>2</sub> were examined. When a solution containing both C<sub>4</sub>(NC)<sub>2</sub> (0.82 mM in 1.0 mL solution for a 1.0 mM total concentration of C<sub>4</sub>(NC)<sub>2</sub>) and *n*-C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C (2.0 mM) was contacted with 200 mg of Au powder previously saturated with C<sub>4</sub>(NC)<sub>2</sub>, only C<sub>4</sub>(NC)<sub>2</sub> was observed on the surface by DRIFTS at all settling times (5 s to 48 h). When a 1.0 mL solution containing both C<sub>4</sub>(NC)<sub>2</sub> (1.0 mM) and *n*-C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C (2.0 mM) was added to 200 mg of clean Au powder, 33% of the

isocyanide on the surface at 5 s and 1 min settling times was  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$ , but at times from 10 min to 48 h, only  $\text{C}_4(\text{NC})_2$  was detected on the Au powder. When a solution containing both  $\text{C}_4(\text{NC})_2$  (1.0 mM) and  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  (1.76 mM in 1.0 mL solution for a 2.0 mM total concentration of  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$ ) was added to 200 mg of Au powder previously saturated with  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$ , 33% of the  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  was displaced by  $\text{C}_4(\text{NC})_2$  after 10 s; 60% was displaced at 10 min, and it was completely displaced by  $\text{C}_4(\text{NC})_2$  after 90 min. Thus, 33% of the  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  was displaced very rapidly (10 s), while the displacement of the remaining  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  by  $\text{C}_4(\text{NC})_2$  took significantly longer (90 min). This is the same pattern that was observed with the diisocyanide  $m\text{-xylyl}(\text{N}^{13}\text{C})_2$ ; 33-39% is displaced relatively rapidly by  $\text{C}_4(\text{NC})_2$  and the remainder is displaced undetectably slowly. However, the displacement of the monoisocyanide ( $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$ ) is much faster than the diisocyanide ( $m\text{-xylyl}(\text{N}^{13}\text{C})_2$ ) displacement in both regimes. For the initial 33-39%,  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  displacement occurs within 10 s while  $m\text{-xylyl}(\text{N}^{13}\text{C})_2$  requires 4 h. For the remaining 67-61%,  $n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$  is completely displaced in 1.5 h while no  $m\text{-xylyl}(\text{N}^{13}\text{C})_2$  is displaced, even after 120 h.

## Discussion

**Saturation Coverages ( $n_{1s}$ ) for Di- and Triisocyanides on Au Powder.** In a previous study<sup>13</sup> of  $n$ -alkylisocyanides on Au powder, it was established that  $n\text{-C}_4\text{H}_9\text{NC}$  is able to achieve a saturation surface coverage ( $n_{1s}$ ) of  $1.53 \times 10^{-6}$  mol  $\text{RNC}/\text{g}_{\text{Au}}$  while the longer chain  $n\text{-C}_{18}\text{H}_{37}\text{NC}$  had a slightly higher  $n_{1s}$  value,  $1.77 \times 10^{-6}$  mol  $\text{RNC}/\text{g}_{\text{Au}}$ . For these same isocyanides in the present study, the  $n_{1s}$  values (Table 2) were slightly lower,  $1.1 \times 10^{-6}$  and  $1.2 \times 10^{-6}$  mol  $\text{RNC}/\text{g}_{\text{Au}}$ ,

respectively, because of the smaller Au powder surface area (0.29 vs. 0.33 m<sup>2</sup>/g<sub>Au</sub>). For the series of CN-(CH<sub>2</sub>)<sub>x</sub>-NC isocyanides, the saturation surface coverage ( $n_{1s}$ ) is lowest for the longest chain derivative, C<sub>12</sub>(NC)<sub>2</sub>. Its  $n_{1s}$  value (Table 2) is  $0.50 \times 10^{-6}$  mol RNC/g<sub>Au</sub>, which corresponds to  $1.0 \times 10^{-6}$  mol -NC groups/g<sub>Au</sub>. Thus, approximately the same number of -NC groups adsorb on the Au powder surface at saturation coverage for *n*-C<sub>4</sub>H<sub>9</sub>NC and C<sub>12</sub>(NC)<sub>2</sub>. This presumably means that the diisocyanide is not adsorbed in a way that stretches the -(CH<sub>2</sub>)<sub>12</sub>- chain across the surface, but instead is kinked (Chart 2) such that the arrangement of the -NC groups is similar to that for *n*-alkylisocyanides on Au powder. However, it should be noted that the arrangement of *n*-alkylisocyanides on Au powder has not been established.

As the -(CH<sub>2</sub>)<sub>x</sub>- chain length becomes shorter, the number of -NC groups that adsorb to the surface per gram of Au increases: C<sub>12</sub>(NC)<sub>2</sub> (1.0) < C<sub>8</sub>(NC)<sub>2</sub> (1.1) < C<sub>6</sub>(NC)<sub>2</sub> (1.3) < C<sub>4</sub>(NC)<sub>2</sub> (1.8) < C<sub>2</sub>(NC)<sub>2</sub> (2.4). The shortest-chain diisocyanide C<sub>2</sub>(NC)<sub>2</sub> has twice as many -NC groups on the surface at saturation coverage as the monoisocyanides *n*-C<sub>4</sub>H<sub>9</sub>NC and *n*-C<sub>18</sub>H<sub>37</sub>NC. This requires that the arrangement of the -NC groups on the Au must be different for C<sub>2</sub>(NC)<sub>2</sub> and the monoisocyanides. These different arrangements are not apparent in the DRIFT  $\nu(\text{NC})$  values as they are essentially the same for *n*-C<sub>18</sub>H<sub>37</sub>NC (2218 cm<sup>-1</sup>) and C<sub>2</sub>(NC)<sub>2</sub> (2216 cm<sup>-1</sup>) (Table 1). Also, the geometry of the C<sub>2</sub>(NC)<sub>2</sub> adsorbate requires an angular attachment (Chart 2) of the isocyanide groups to the surface, but this attachment does not significantly affect the  $\nu(\text{NC})$  value of C<sub>2</sub>(NC)<sub>2</sub> as compared with the other isocyanides (Table 1). While Au powder is presumed to have a predominantly (111) surface, this

has not been established experimentally; we therefore do not speculate on the arrangement of the -NC groups on the surface.

As for the  $\text{CN}-(\text{CH}_2)_x\text{-NC}$  adsorbates, both -NC groups in the xylyldiisocyanides, *m*-xylyl(NC)<sub>2</sub> and *p*-xylyl(NC)<sub>2</sub>, are bonded to the surface as established by the position of the  $\nu(\text{NC})$  bands (Table 1) and the absence of  $\nu(\text{NC})$  absorptions corresponding to uncoordinated isocyanide groups. The  $n_{1s}$  value for *m*-xylyl(NC)<sub>2</sub> ( $0.93 \times 10^{-6}$  mol RNC/g<sub>Au</sub>) is slightly larger than that for the *p*-xylyl(NC)<sub>2</sub> isomer ( $0.84 \times 10^{-6}$  mol RNC/g<sub>Au</sub>), which is perhaps related to the orientation of the arene ring and the space that it requires over the surface. The observation that both the *m*- and *p*-xylyldiisocyanides adsorb more -NC groups (1.9 and 1.7 mole -NC groups/g<sub>Au</sub>, respectively) than the monoisocyanides ( $1.2 \times 10^{-6}$ ) suggests that the arene rings do not cover a significant portion of the surface or *n*-C<sub>18</sub>H<sub>37</sub>NC and *n*-C<sub>4</sub>H<sub>9</sub>NC are not densely packed on the Au surface.

The tridentate isocyanides, Tripod and Tren, adsorb through all three of their -NC groups and achieve surface coverages ( $1.0 \times 10^{-6}$  and  $0.8 \times 10^{-6}$  mol -NC groups/g<sub>Au</sub>) that are about the same as or slightly less than those of the monoisocyanides. They do not exhibit the dense packing of C<sub>2</sub>(NC)<sub>2</sub> ( $2.4 \times 10^{-6}$  mol -NC groups/g<sub>Au</sub>), and their DRIFT spectra (Table 1) on Au exhibit  $\nu(\text{NC})$  values that are comparable to those of the mono- and diisocyanides.

#### **Kinetic Effects on the Competitive Adsorption of Two Isocyanides on Au**

**Powder.** As described in the Results section and in Figures 1 and 2, when Au powder (200 mg) saturated with *m*-xylyl(N<sup>13</sup>C)<sub>2</sub> is treated with 1.0 mL of a DCE solution containing 1.0 mM *m*-xylyl(NC)<sub>2</sub> or C<sub>4</sub>(NC)<sub>2</sub> and sufficient

$m$ -xylyl( $N^{13}C$ )<sub>2</sub> to give the same number of moles of this  $^{13}C$ -labeled isocyanide, only 34-39% of the  $m$ -xylyl( $N^{13}C$ )<sub>2</sub> is displaced after approximately 4 h but no further displacement occurs, even after 120 h. These and related experiments (see Results) show that 34-39% of the total adsorbed isocyanide ( $S_{\text{Total}} = S_a + S_b$ ) undergoes relatively rapid (< 4 h) exchange with a second isocyanide in solution. The remaining 61-66% of the initially adsorbed isocyanide is kinetically inert to exchange under these conditions. These two distinctly different rates of isocyanide exchange appear to correspond to the two regimes that were identified in solution studies<sup>13</sup> of the adsorption of  $n$ -alkylisocyanides ( $R-N\equiv C$ ) on Au powder. In the low coverage regime (< 70% of  $n_{1s}$ ), equilibrium constants (eq 1) for monoisocyanide adsorption ( $K_1 > 10^6$ ) were high and  $\nu(NC)$  values for the adsorbed species were at least 8  $cm^{-1}$  higher than those observed for coverages above 70% of  $n_{1s}$ . Also, in the high coverage regime (> 70%  $n_{1s}$ ), the  $K_1$  values ( $1.8 \times 10^4$  -  $2.4 \times 10^4$ ) were substantially smaller than those at low coverage. It appears that the  $m$ -xylyl( $N^{13}C$ )<sub>2</sub> adsorbed in the high coverage regime undergoes exchange while  $m$ -xylyl( $N^{13}C$ )<sub>2</sub> at low coverage (< 70%  $n_{1s}$ ) does not exchange with solution isocyanide under these conditions.

In order to determine if a monoisocyanide undergoes exchange more rapidly than the diisocyanide,  $m$ -xylyl( $N^{13}C$ )<sub>2</sub>, Au powder (200 mg) saturated with  $n$ -C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C was treated with a 1.0 mL DCE solution containing both  $n$ -C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C (2.0 mM) and C<sub>4</sub>(NC)<sub>2</sub> (1.0 mM), 33% of the  $n$ -C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C was displaced by C<sub>4</sub>(NC)<sub>2</sub> within 10 s, but 60% displacement required 10 min, and complete displacement of the  $n$ -C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C occurred within 90 min. Thus, in both the high and low coverage regimes, the monoisocyanide,  $n$ -C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C, is

displaced more rapidly than the diisocyanide,  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub>. In the high coverage regime, C<sub>4</sub>(NC)<sub>2</sub> displacement of  $n$ -C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C occurs within 10 s while  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> requires 4 h. In the low coverage regime,  $n$ -C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C is displaced in 1.5 h, while  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> is not displaced even after 120 h.

While the experimental results in Figures 1 and 2 show that only 33% of  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> is displaced by  $m$ -xylyl(NC)<sub>2</sub> (1.0 mL of a 1.0 mM DCE solution) also containing sufficient  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> to give equal amounts of the two isocyanides even after 120 h, it is possible to displace all of the  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> with higher concentrations of  $m$ -xylyl(NC)<sub>2</sub>. If the concentration of the 1.0 mL solution of  $m$ -xylyl(NC)<sub>2</sub> is increased to 5.0 mM (the  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> concentration remains the same), 63% of the  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> is displaced within 4 h; 72% is displaced within 4 h with a 10.0 mM solution and 100% is displaced within 4 h with a 20.0 mM solution. These experiments demonstrate that while only 33% of the  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> is displaced at 1.0 mM  $m$ -xylyl(NC)<sub>2</sub>, more and more of the adsorbed isocyanide is displaced within a 4 h period as the concentration of the displacing  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> ligand is increased up to 20.0 mM where all of the  $m$ -xylyl(N<sup>13</sup>C)<sub>2</sub> is displaced. Thus, even the strongly adsorbed isocyanide in the low coverage regime can be displaced and the rate of this displacement depends on the concentration of the displacing  $m$ -xylyl(NC)<sub>2</sub>.

The relative binding affinities ( $Q_{ab}$ ) of pairs of isocyanides were determined by adding 1.0 mL of a DCE solution containing both of the isocyanides to 200 mg of Au powder. After being allowed to stand for at least

12 h, the measured amounts of the isocyanides in solution and on the Au were used to calculate the relative  $Q_{ab}$  values (eq 2-7) in Table 3. For the adsorption of the *m*-xylyl( $N^{13}C$ )<sub>2</sub> and C<sub>4</sub>(NC)<sub>2</sub> pair of isocyanides, Figure 2 shows that C<sub>4</sub>(NC)<sub>2</sub> adsorbs more quickly than *m*-xylyl( $N^{13}C$ )<sub>2</sub> but some of it is displaced to give steady-state amounts of the isocyanides on the Au and in solution within approximately 4 h. The  $Q_{ab}$  values are measured at times (> 12 h) when the system has reached steady-state. It is not known, however, whether or not the system (eq 2-4) is at equilibrium. Based on the kinetic studies discussed above, we would expect that the isocyanide that adsorbs first on the surface (C<sub>4</sub>(NC)<sub>2</sub> in this case), up to 61-66% coverage (low coverage regime) would not undergo exchange with the isocyanides in solution; only the most weakly adsorbed isocyanide at coverages above 61-66% (high coverage regime) would equilibrate with the isocyanide in solution during the 12 h settling time. Because of the kinetic inertness of the isocyanides in the low coverage regime, the measured  $Q_{ab}$  values are probably not equilibrium constants. Also, as noted in Table 4, these values are not constant for a range of concentrations; however, the dependence of  $Q_{ab}$  on concentration is not large, which suggests that the  $Q_{ab}$  values are useful, semi-quantitative measures of the binding affinities of mono-, di-, and triisocyanides.

**Mono-, Di-, and Triisocyanide Binding Affinities ( $Q_{ab}$ ) for Au Powder.** Since the relative  $Q_{ab}$  values (Table 3) for the mono- and triisocyanides depend on the solution concentration units (e.g., mM or M) that are used in eqs 5 and 7, a quantitative comparison of the relative binding affinities of the mono-, di-, and triisocyanides based on their  $Q_{ab}$  values is not useful. However, other evidence



supports the trend in  $Q_{ab}$  values which indicate that, in general, the binding affinities of these ligands increase with the number of -NC donor groups in them:  $RNC < R(NC)_2 < R(NC)_3$ . Evidence that the diisocyanide,  $C_{12}(N^{13}C)_2$ , binds more strongly than the monoisocyanide  $n\text{-}C_{18}H_{37}NC$  comes from an experiment in which a solution containing equal concentrations (1.0 mM) of the two isocyanides were contacted with 200 mg of Au powder for 12 h. More than 90% of the surface was covered with  $C_{12}(N^{13}C)_2$  and only traces of  $n\text{-}C_{18}H_{37}NC$  were present. When a solution containing a 5.0 mM/1.0 mM ratio of  $n\text{-}C_{18}H_{37}NC/C_{12}(N^{13}C)_2$  was contacted with clean Au powder, the  $n\text{-}C_{18}H_{37}NC/C_{12}(N^{13}C)_2$  ratio on the surface was 1.9. That the triisocyanide,  $\text{Tripod}(NC)_3$ , binds more strongly than the diisocyanide,  $m\text{-xylyl}(N^{13}C)_2$ , is evident from the experiment in which a DCE solution containing 1.0 mM  $m\text{-xylyl}(N^{13}C)_2$  and only 0.67 mM  $\text{Tripod}(NC)_3$  is contacted with Au (200 mg). Despite the lower concentration of  $\text{Tripod}(NC)_3$  in solution, it is the predominant (60%) isocyanide adsorbed on the Au.

In an earlier study,<sup>13</sup> we observed that  $K_1$  values (eq 1) for the adsorption of  $n$ -alkylisocyanides on Au powder depend only slightly on the length of the  $n$ -alkyl chain; for example, competitive adsorption of equimolar  $n\text{-}C_{18}H_{37}N^{13}C$  and  $n\text{-}C_4H_9NC$  in DCE solution produced a  $n\text{-}C_{18}H_{37}N^{13}C/n\text{-}C_4H_9NC$  equilibrium ratio of only 4.1 on the Au surface. In the present studies of diisocyanides, the binding affinities ( $Q_{ab}$ ) increase with a decrease in the length of the  $-(CH_2)_x$ - chain:  $C_{12}(NC)_2$  (0.022)  $<$   $C_8(NC)_2$  (0.060)  $<$   $C_6(NC)_2$  (0.092)  $<$   $C_4(NC)_2$  (1.0)  $<$   $C_2(NC)_2$  (1.4). These results show that the  $Q_{ab}$  of  $C_2(NC)_2$  is 64 times larger than that of  $C_{12}(NC)_2$ , and the binding affinity of diisocyanides is

much more sensitive to the chain length than the monoisocyanides. As noted in the saturation coverage ( $n_{1s}$ ) discussion, the chain is presumably kinked (Chart 2) in  $C_{12}(NC)_2$  to give a surface coverage of -NC groups that is nearly the same as that of the monoisocyanides. The short-chain diisocyanides, especially  $C_2(NC)_2$ , are unable to kink but they adsorb much more strongly than their long-chain analogs. Perhaps it is the greater loss of entropy that accompanies the adsorption of long-chain diisocyanides from solution that accounts for their less favorable adsorption. The lower  $Q_{ab}$  values for the long-chain diisocyanides may also be influenced by kinetic factors. When a diisocyanide adsorbs through only one -NC group, it is still labile on the entire Au powder surface under the conditions of the  $Q_{ab}$  measurements, as discussed in the previous section. However, once both -NC groups are bound, the ligand is no longer able to exchange with isocyanide in solution on the low coverage (up to 61-66%) portion of the surface. Thus, the rate of conversion of mono-coordinated to di-coordinated diisocyanide could control the amount of a given diisocyanide on the kinetically inert 61-66% portion of the surface. It is likely that the short-chain diisocyanides will bind their second -NC groups to the surface faster than the long-chain derivatives. Thus, if kinetic factors affect  $Q_{ab}$ , they will favor adsorption of the short-chain diisocyanides.

The *m*- and *p*-xylyl( $NC$ )<sub>2</sub> diisocyanides have  $Q_{ab}$  values, 1.0 and 0.17, respectively, that are similar to those of  $C_4(NC)_2$  (1.0) and  $C_6(NC)_2$  (0.092). All four ligands have approximately the same number of carbon atoms (4-6) linking their -NC groups, which may account for their similar binding affinities. Although the xylyl( $NC$ )<sub>2</sub> ligands are structurally different than the

CN-(CH<sub>2</sub>)<sub>x</sub>-NC diisocyanides, their similar  $Q_{ab}$  values suggest that there is no direct interaction between the arene group and the Au surface.

Of the two triisocyanide ligands, Tripod(NC)<sub>3</sub> has the higher  $Q_{ab}$  value (1.5). Tripod(NC)<sub>3</sub> was chosen for study because it forms a very stable complex with the triangle of Os atoms in Os<sub>3</sub>(CO)<sub>9</sub>[Tripod(NC)<sub>3</sub>].<sup>15a</sup> Since the Os-Os distance (2.86 Å) in this triangle is very similar to the Au-Au distance (2.88 Å) on Au (111), it was expected that Tripod(NC)<sub>3</sub> would bind unusually strongly. However, this was not observed in the  $Q_{ab}$  values. The other triisocyanide, Tren(NC)<sub>3</sub>, does not have a structure that matches Au-Au distances on Au(111). With 5 atoms (four C and one N) linking two -NC groups, this ligand has structural features similar to those in *m*-xylyl(NC)<sub>2</sub>, and its  $Q_{ab}$  (1.2) is only slightly larger than that (1.0) of *m*-xylyl(NC)<sub>2</sub>. Other evidence that Tren(NC)<sub>3</sub> binds only slightly more strongly *m*-xylyl(N<sup>13</sup>C)<sub>2</sub> was obtained from the experiment in which a DCE (1.0 mL) solution containing 1.0 mM of both *m*-xylyl(N<sup>13</sup>C)<sub>2</sub> and Tren(NC)<sub>3</sub> was contacted with Au (200 mg). Despite equal concentrations of the isocyanides in solution, there is only marginally more Tren(NC)<sub>3</sub> (55%) than *m*-xylyl(N<sup>13</sup>C)<sub>2</sub> (45%) on the surface.

### Summary

Adsorption studies of the di- and triisocyanides in Chart 1 on Au powder show that all of the -N≡C groups are bound to Au atoms. The number of moles of the short-chain diisocyanide C<sub>2</sub>(NC)<sub>2</sub> adsorbed at saturation coverage ( $n_{1s}$ ) is equal to that of the monoisocyanide *n*-C<sub>18</sub>H<sub>37</sub>NC (Table 2); this means that twice as many -N≡C groups are bound to the surface with C<sub>2</sub>(NC)<sub>2</sub> than

$n\text{-C}_{18}\text{H}_{37}\text{NC}$ . For the  $\text{C}\equiv\text{N}-(\text{CH}_2)_x-\text{N}\equiv\text{C}$  diisocyanides, the saturation coverage values ( $n_{1s}$ ) decrease as the linking  $-(\text{CH}_2)_x-$  group lengthens from  $x = 2$  to  $x = 12$ . The number of moles of  $-\text{N}\equiv\text{C}$  groups coordinated for  $\text{C}_{12}(\text{NC})_2$  is essentially the same as that for the monoisocyanide  $n\text{-C}_{18}\text{H}_{37}\text{NC}$ . Kinetic measurements show that all of the monoisocyanide  $n\text{-C}_{18}\text{H}_{37}\text{NC}$  adsorbed on Au powder is displaced by  $\text{C}_4(\text{NC})_2$  within 90 m. However, only 39% of the diisocyanide  $m\text{-xylyl}(\text{N}^{13}\text{C})_2$  is displaced by  $\text{C}_4(\text{NC})_2$  even after 120 h (Fig 2). This result, together with those of other experiments, demonstrate that only 34-39% of the diisocyanide  $m\text{-xylyl}(\text{N}^{13}\text{C})_2$  is exchangeable while the remaining 61-66% of the diisocyanide is kinetically inert to exchange under these conditions. This kinetic inertness made it impossible to measure equilibrium constants for the competitive adsorption of two isocyanides on Au powder (eq 2-4). However,  $Q_{ab}$  values, which probably include both kinetic and thermodynamic factors, have been determined (Table 3). In general, the binding affinities of the isocyanides increase with the number of  $-\text{NC}$  donor groups on the ligands ( $\text{RNC} < \text{R}(\text{NC})_2 < \text{R}(\text{NC})_3$ ). For the diisocyanides, the  $Q_{ab}$  values increase significantly as the  $-(\text{CH}_2)_x-$  link between the  $-\text{NC}$  groups becomes shorter; both thermodynamic and kinetic arguments account for this trend. Because of its structure, the  $\text{C}_2(\text{NC})_2$  ligand is presumably forced to bind to the Au surface with the  $-\text{NC}$  groups tilted away from the surface normal (Chart 2). Despite this geometry, it has the highest binding affinity ( $Q_{ab}$ ) and highest saturation coverage ( $n_{1s}$ ) of any of the  $\text{CN}-(\text{CH}_2)_x-\text{NC}$  ligands. DRIFTS studies of these ligands on Au powder show that the positions ( $\text{cm}^{-1}$ ) of their  $\nu(\text{NC})$  absorptions (Table 1) are very similar, even for  $\text{C}_2(\text{NC})_2$ , which suggests

that each of the -NC groups binds through the carbon to a single Au surface atom.

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**Table 1. Infrared Data for the Isocyanides in DCE and on Au Powder**

Isocyanide	$\epsilon^a$ , $M^{-1}cm^{-1}$	$\nu(NC)^a$ , $cm^{-1}$	DRIFTS $\nu(NC)^b$ , $cm^{-1}$
<i>n</i> -C <sub>4</sub> H <sub>9</sub> NC	246±3	2150	2225
<i>n</i> -C <sub>18</sub> H <sub>37</sub> NC	241±3	2150	2218
C <sub>2</sub> (NC) <sub>2</sub>	657±8	2152	2216
C <sub>4</sub> (NC) <sub>2</sub>	521±3	2150	2217
C <sub>6</sub> (NC) <sub>2</sub>	521±3	2150	2215
C <sub>8</sub> (NC) <sub>2</sub>	523±4	2150	2218
C <sub>12</sub> (NC) <sub>2</sub>	525±4	2150	2219
<i>m</i> -xylyl(NC) <sub>2</sub>	523±3	2150	2220
<i>p</i> -xylyl(NC) <sub>2</sub>	525±5	2150	2213
Tripod(NC) <sub>3</sub>	758±8	2147	2222
Tren(NC) <sub>3</sub>	751±7	2150	2229
<i>m</i> -xylyl(N <sup>13</sup> C) <sub>2</sub>	524±4	2115	2187
C <sub>12</sub> (N <sup>13</sup> C) <sub>2</sub>	522±4	2111	2182
<i>n</i> -C <sub>18</sub> H <sub>37</sub> N <sup>13</sup> C	244±3	2113	2187

<sup>a</sup> In DCE solvent.<sup>b</sup> DRIFTS of Au powder with saturation coverage of the isocyanide.

**Table 2. Amounts of the Isocyanides Adsorbed on Au Powder at Saturation Coverage ( $n_{1s}$ )**

Isocyanide	$n_{1s}$ (mol/g <sub>Au</sub> ) $\times 10^6$
$n\text{-C}_{18}\text{H}_{37}\text{NC}$	1.2 $\pm$ 0.1
$n\text{-C}_4\text{H}_9\text{NC}$	1.1 $\pm$ 0.1
$\text{C}_2(\text{NC})_2$	1.2 $\pm$ 0.1
$\text{C}_4(\text{NC})_2$	0.90 $\pm$ 0.03
$\text{C}_6(\text{NC})_2$	0.63 $\pm$ 0.04
$\text{C}_8(\text{NC})_2$	0.55 $\pm$ 0.04
$\text{C}_{12}(\text{NC})_2$	0.50 $\pm$ 0.02
$m\text{-xylyl}(\text{NC})_2$	0.93 $\pm$ 0.04
$p\text{-xylyl}(\text{NC})_2$	0.84 $\pm$ 0.04
Tripod( $\text{NC}$ ) <sub>3</sub>	0.34 $\pm$ 0.03
Tren( $\text{NC}$ ) <sub>3</sub>	0.26 $\pm$ 0.03
$m\text{-xylyl}(\text{N}^{13}\text{C})_2$	0.90 $\pm$ 0.04
$\text{C}_{12}(\text{N}^{13}\text{C})_2$	0.53 $\pm$ 0.02
$n\text{-C}_{18}\text{H}_{37}\text{N}^{13}\text{C}$	1.2 $\pm$ 0.1



**Table 3. Measured and Relative  $Q_{ab}$  Values (eq 2-7) for the Competitive Adsorption of RNC,  $R(NC)_2$ , and  $R(NC)_3$  on Au Powder from DCE Solvent**

Isocyanide (a)	$C_a/C_b$ mM/mM	Measured $Q_{ab}$	Relative $Q_{ab}^d$
Tripod(NC) <sub>2</sub>	1.0/1.0 <sup>a</sup>	1.5 <sup>a</sup>	1.5
C <sub>2</sub> (NC) <sub>2</sub>	1.0/1.0 <sup>a</sup>	1.4 <sup>a</sup>	1.4
Tren(NC) <sub>3</sub>	1.0/1.0 <sup>a</sup>	1.2 <sup>a</sup>	1.2
C <sub>4</sub> (NC) <sub>2</sub>	1.0/1.0 <sup>a</sup>	1.0 <sup>a</sup>	1.0
<i>m</i> -xylyl(NC) <sub>2</sub>	1.0/1.0 <sup>a</sup>	1.0 <sup>a</sup>	1.0
<i>p</i> -xylyl(NC) <sub>2</sub>	4.0/1.0 <sup>a</sup>	0.17 <sup>a</sup>	0.17
C <sub>6</sub> (NC) <sub>2</sub>	4.0/1.0 <sup>a</sup>	0.092 <sup>a</sup>	0.092
C <sub>8</sub> (NC) <sub>2</sub>	8.0/1.0 <sup>a</sup>	0.060 <sup>a</sup>	0.060
C <sub>12</sub> (NC) <sub>2</sub>	10.0/1.0 <sup>a</sup>	0.022 <sup>a</sup>	0.022
<i>n</i> -C <sub>18</sub> H <sub>37</sub> NC	5.0/1.0 <sup>b</sup>	0.076 <sup>b</sup>	0.0017
<i>n</i> -C <sub>4</sub> H <sub>9</sub> NC	1.0/1.0 <sup>c</sup>	0.24 <sup>c</sup>	0.00041

<sup>a</sup> b = *m*-xylyl(N<sup>13</sup>C)<sub>2</sub>.

<sup>b</sup> b = C<sub>12</sub>(N<sup>13</sup>C)<sub>2</sub>.

<sup>c</sup> b = *n*-C<sub>18</sub>H<sub>37</sub>N<sup>13</sup>C.

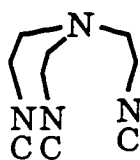
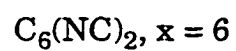
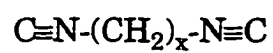
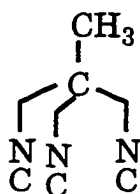
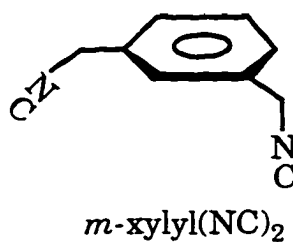
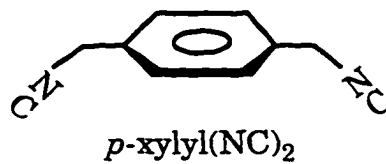
<sup>d</sup>  $Q_{ab}$  relative to *m*-xylyl(N<sup>13</sup>C)<sub>2</sub>.

**Table 4. Measured  $Q_{ab}$  Values (eq 3 and 6) for the Competitive Adsorption of  $C_6(NC)_2$  (a) and  $m$ -xylyl( $N^{13}C$ )<sub>2</sub> (b) on Au Powder from DCE Solvent with Increasing Concentrations of  $C_6(NC)_2$**

$C_a$ , mM	Measured $Q_{ab}$
4.0	0.092
6.0	0.087
8.0	0.059
10.0	0.052
20.0	0.049
30.0	0.047
50.0	0.040
80.0	<sup>b</sup>

<sup>a</sup>  $C_b = 1.00$  mM for all measurements.

<sup>b</sup> No  $m$ -xylyl was observed on the Au powder using DRIFTS.

**Chart 1**Tren(NC)<sub>3</sub>Tripod(NC)<sub>3</sub>

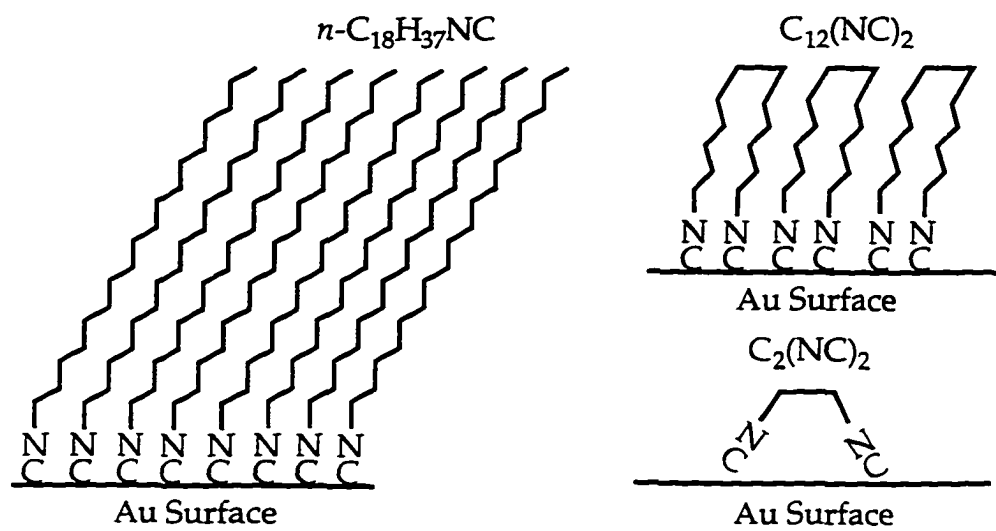
**Chart 2**

Figure 1. Surface ratio  $S_b/S_{\text{Total}}$  ( $a = m\text{-xylyl}(\text{NC})_2$  and  $b = m\text{-xylyl}(\text{N}^{13}\text{C})_2$ ) vs. solution contact time (h), where  $S_a + S_b = S_{\text{Total}}$ .

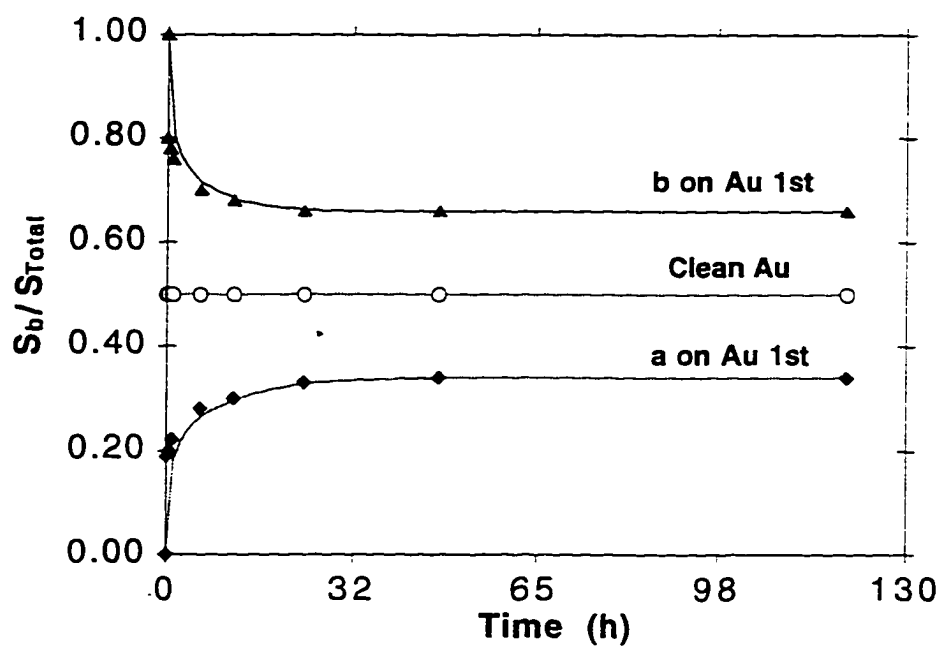
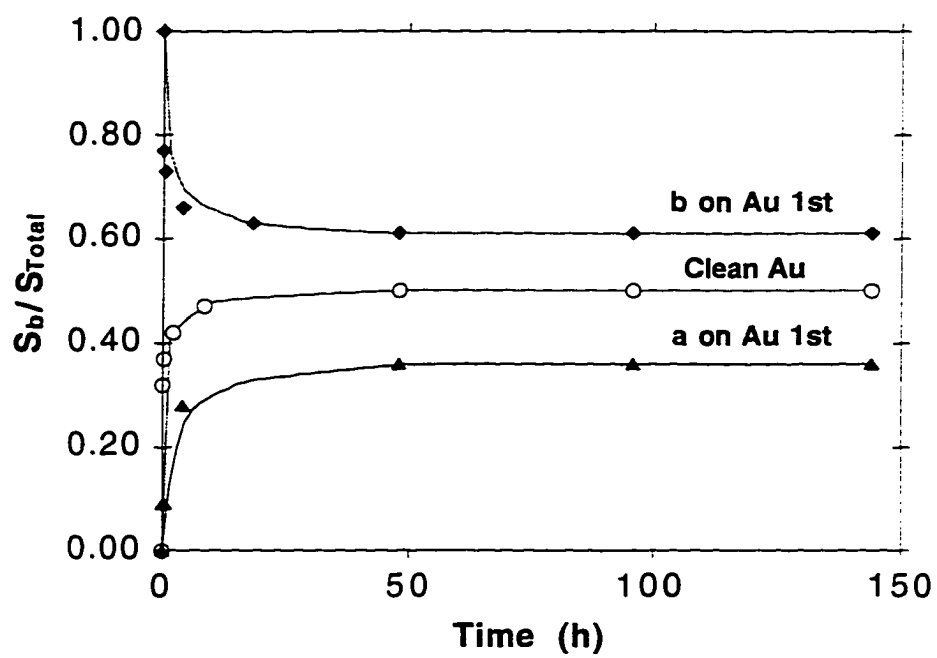


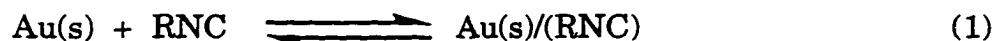
Figure 2. Surface ratio  $S_b/S_{\text{Total}}$  ( $a = \text{C}_4(\text{NC})_2$  and  $b = m\text{-xylyl}(\text{N}^{13}\text{C})_2$ ) vs. solution contact time (h), where  $S_a + S_b = S_{\text{Total}}$ .



## GENERAL SUMMARY

Self-assembled monolayers (SAM's) have been a subject of great interest during the past decade. Driving this period of discovery is the relevance of SAM's to biological interfaces and membranes, corrosion inhibition, electrochemistry, wetting, adhesion, and microelectronic circuitry. One particularly successful system, *n*-alkylthiolates on Au film, has been a major focus due to its ease of preparation, high thermal stability and the availability of several methods for characterization. Like *n*-alkylthiolates, *n*-alkylisocyanides (R-N[C]) have variable length *n*-alkyl chains but with a quite different surface-binding head group.

Our group has previously shown that isocyanides are readily adsorbed from solutions to Au powder and bind to the Au surface in an end-on fashion through the terminal carbon. A later report demonstrated that the equilibrium constants for the reversible adsorption (eq 1) of electronically inequivalent isocyanides could be obtained using the Langmuir isotherm technique.



Initially, several alkylisocyanides ( $\text{RNC} = n\text{-C}_4\text{H}_9\text{NC}$  ( $\text{C}_4\text{NC}$ ),  $n\text{-C}_6\text{H}_{13}\text{NC}$  ( $\text{C}_6\text{NC}$ ),  $n\text{-C}_8\text{H}_{17}\text{NC}$  ( $\text{C}_8\text{NC}$ ),  $n\text{-C}_{12}\text{H}_{25}\text{NC}$  ( $\text{C}_{12}\text{NC}$ ), and  $n\text{-C}_{18}\text{H}_{37}\text{NC}$  ( $\text{C}_{18}\text{NC}$ )) were synthesized to examine the effect of tail length on Au powder adsorption.<sup>3</sup> It was observed that the length of the alkyl chain affected not only the Au

surface binding affinity, but also the rate of surface saturation and saturation coverage values. Direct competition studies were also studied using a  $^{13}\text{C}$  labeled isocyanide ( $\text{C}_{18}\text{NC}^*$ ). These studies demonstrated the stabilization afforded by substrate-substrate packing forces in SAM's formed by the longer chain isocyanides.

In a second study, di and triisocyanides were synthesized to determine the effect that the length of the connecting link (i.e. # of  $(-\text{CH}_2-)$  groups) and the number of isocyanide groups (as points of attachment) have on Au adsorption stability. Reports have shown that diisocyanides with flexible backbones such as  $\text{C}\equiv\text{N}-(\text{CH}_2)_6-\text{N}\equiv\text{C}$  and  $\text{C}\equiv\text{N}-(\text{CH}_2)_{12}-\text{N}\equiv\text{C}$  bind to Au through both  $-\text{N}\equiv\text{C}$  groups producing a SAM with a smaller ellipsometric thickness than a diisocyanide with an inflexible backbone such as 1,4-phenylene-diisocyanide. Our work in this area describes the binding modes, relative binding affinities ( $Q_{\text{ab}}$ ) and surface coverage values for a series of flexible alkyl and xilyldiisocyanides on Au powder surfaces.



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